UNUSUAL INTRAMOLECULAR KINETIC ISOTOPE EFFECTS:

SELECTIVITY BEYOND TRANSITION STATE THEORY'S JURISDICTION

A Dissertation

by

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Submitted to the Office of Graduate and Professional Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

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December 2014

Major Subject: Chemistry

ABSTRACT

The nature of non-statistical dynamic Kinetic Isotope Effects for a series of ordinary organic reactions is studied throughout this dissertation. A combination of experimental intramolecular KIEs using NMR methodology with computational calculations was employed in order to shed light about the selectivity in the Diels-Alder dimerization of methacrolein and cyclopentadienone, the iminium catalyzed Diels-Alder between cyclopentadiene and *trans*-cinnamaldehyde and the cleavage of alkoxy radicals.

Newtonian isotope effects as the underlying physical phenomena behind the KIEs in the thermal dimerization of methcrolein was studied. The temperature dependence of these novel form of KIEs was investigated by analyzing the isotopic distribution at dicyclopentadienone prepared at low and high temperatures. It was shown that Newtonian KIEs are temperature independent over a range of 100 degress.

The non-statistical behavior in the cleavage of alkoxy radicals has been investigated. These highly reactive intermediates are prone to behave in a non-statistical fashion due to their excess energy. The opening of 1-methylcyclopentoxy radical has shown that heavy-atom tunneling can play an important role even at elevated temperatures. As the barrier for the cleavage for alkoxy radicals is decreased, other dynamic effects start to impact the selectivity of this reaction in ways that TST cannot account for.

On the iminium catalyzed Diels-Alder reaction between cyclopentadiene and *trans*-cinnamaldehyde, computational calculations support a two steps cycloaddition on the free energy surface and a "seemingly concerted" reaction in potential energy. The role of non-statistical recrossing for this cycloaddition was investigated experimentally by measuring intramolecular KIEs.

DEDICATION

This dissertation is dedicated to my mother Lina De Sanctis, whose love, guidance and encouragement through life have greatly inspired me to always pursue my goals. To my husband, Fernando Aponte, for his unconditional love and support over the last ten years. Thank you both for bringing happiness into my life.

ACKNOWLEDGEMENTS

I would like to thank my committee chair, Dr. Daniel A. Singleton for his guidance, support and patience throughout the course of this research. I have no words to express my gratitude towards everything you have taught me about chemistry. I would like to thank my committee members, Dr. Gabbai, Dr. Wheeler and Dr. Malavé, for their assistance throughout this work.

Thanks also go to my friend Yatsandra Oyola for her unconditional help and taking care of me when I started this long journey. Thank you for so much in such a short period of time. I also want to extend my gratitude to Zhuo Chen for lenghthy and challenging chemistry conversations. Special Thanks to Kelly Mar Rosa for starting this journey with me and to Krystal Morales for her support when I first arrived to Texas A&M University. I would also like to thank the past members of the Singleton research group for their invaluable contribution to my research.

Finally, thanks to my mother for her encouragement and to my husband, Fernando Aponte, for his patience, support and love.

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CHAPTER I

BACKGROUND AND SIGNIFICANCE

1.1 Kinetic Isotope Effects

The term isotope is derived from the Greeks words "isos" and "topos" that combined mean "same place".[1] In the periodic table all isotopes of an element fall in the same place or position. The term isotope is used to denote variants of a particular element that possesses different nuclear properties but have the same electronic and chemical properties. However, isotopic substitution in a molecule changes the zero-point energy (ZPE), as shown on equations **1.1** and **1.2**.[2]

$$ZPE = \frac{1}{2}\, hv \qquad (\mathbf{1.1})$$

$$v = \frac{1}{2\Pi}\sqrt{\frac{k}{m}} \qquad (\mathbf{1.2})$$

As a result of the difference in vibrational frequencies of isotopologues at the transition state, isotopically substituted molecules tend to react at different rates. This change in rate is referred to as a kinetic isotope effect (KIE). In conventional KIEs, the main contributor to the effects are changes in ZPE, **Figure 1.1**. KIEs are studied because they provide information about the structure of transition states and thereby are an indicator of the mechanism of reactions.

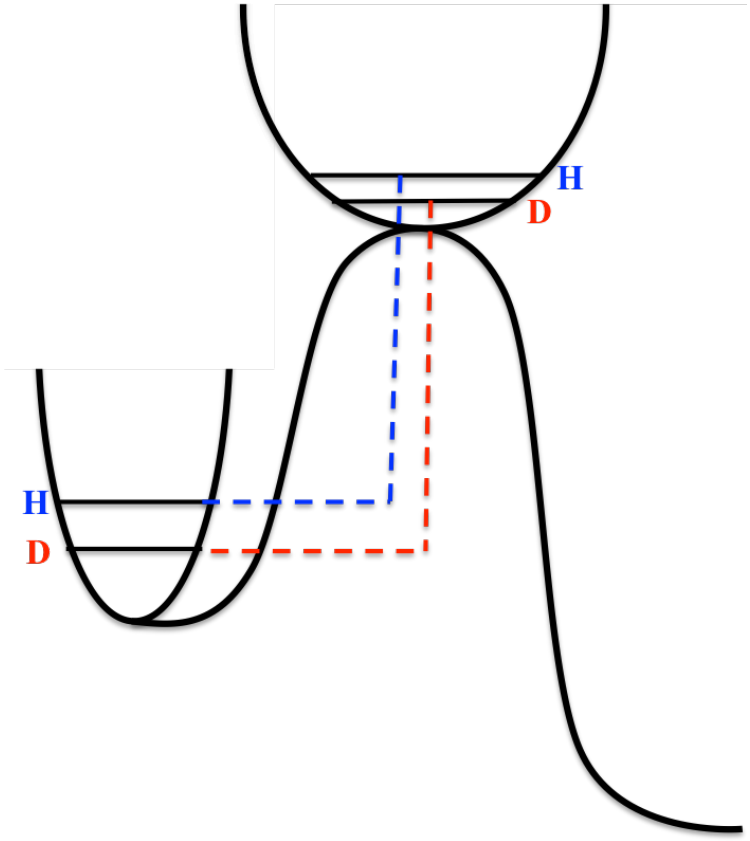

Figure 1.1 The main origin of KIEs is the difference in ZPE between hydrogen (^{1}H) and Deuterium (^{2}H) as reactants approach the transition state of a chemical reaction.

KIEs can be classified as primary or secondary. Primary KIEs refer to the effect observed from isotopic substitution at a position where a sigma-bond is being broken or formed. The origin of primary KIEs is difference in stretching vibrations of isotopes. Secondary KIEs are observed by isotopic substitution at a position that is not involved in sigma-bond forming or breaking. Secondary KIEs originate mainly from changes in the bending vibrations between a ground state and a transition state and the effect of isotope substitution on the ZPE associated with these vibrations. KIEs can also be referred as

normal or inverse. A normal KIE is observed when the position of isotopic substitution is more loosely bound in the transition state than in the starting materials leading to closer energy levels at the transition state. As a result, the lighter isotope reacts faster than the heavier isotope and k_{Light}/k_{Heavy} is greater than 1. An inverse isotope effect on the other hand, is observed when the position of isotopic substitution is more tightly bound in the transition state than in the starting materials resulting in more separated energy levels at the transition state. In these circumstances heavier isotope reacts faster than the lighter one and k_{Light}/k_{Heavy} is smaller than 1. **Figure 1.2** illustrates the primary and secondary KIEs on the decarboxylation of β-keto acids when a label is introduced at different positions of the starting material.

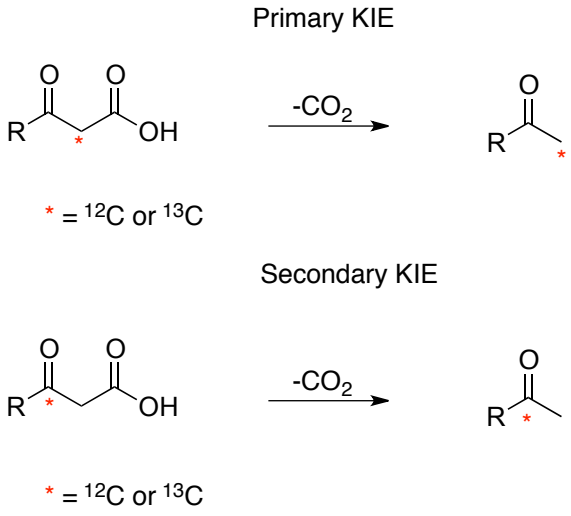

Figure 1.2 Example of primary and secondary KIEs in the decarboxylation of a β-keto acid.

Experimental KIEs can be measured via absolute rate kinetics or competition experiments. In absolute rate kinetics the rate of reaction is measured individually for the

unlabeled and labeled starting material. Although this approach is relatively straightforward, the difference in rates between reactions isotopically labeled can be very small, leading to high uncertainties and at times misleading interpretation of small KIEs. However, this approach is mostly used for measuring large KIEs. Competition experiments can be studied on intramolecular competitions, a pair of positions within a molecule compete to react, or on intermolecular competitions where a pair of starting materials (labeled and unlabeled) compete to react and form products. The main limitation of this approach is that it requires isotopic labeling of starting materials, and this process can be tedious, time consuming, expensive and hard to control in terms of selectivity.

Analytical techniques like mass spectrometry and nuclear magnetic resonance (NMR) have greatly ease the isotopic distribution analysis of organic molecules, and therefore have facilitated the measurement of KIEs at natural abundance. Mass spectrometry is a power technique to determine the isotopic composition of a molecule, even at natural abundance. It requires very small amounts of sample, however the technique is limited to small molecules such as CO_2 that are not complicated by fragmentation. The use of NMR methodology to measure KIEs at natural abundance was explored by several groups[3,4] but only effectively developed as a useful technique by the Singleton group.[5,6] The greatest advantage of this technique is the ability to obtain a complete set of isotope effects in complex organic molecules without labeling. In addition, NMR methodology is a great technique for measuring both intermolecular and intramolecular KIEs.

Intermolecular KIEs provide details about the rate-limiting step of a reaction. Intermolecular KIEs are typically measured by absolute kinetics or competition experiments. Intramolecular KIEs can be used to provide details about the mechanism of steps after the rate-limiting step. Intramolecular KIEs are observed when a structurally symmetrical, but isotopically unsymmetrical molecule breaks its symmetry to afford products of lower symmetry. The step breaking symmetry may be refered to as the product-determining step, so intramolecular KIEs characterize the product-determining step. The combination of intermolecular and intramolecular KIEs is very useful in the detailed study of the mechanism of a chemical reaction and can help to distinguish between a single-step versus a multiple-step mechanism.[6,7] The main limitations of a combined intermolecular/intramolecular KIEs study are the use of a high precision technique that allows the measurement of isotope effects and/or the presence of a large KIE in order to reliably distinguish between both values. The Singleton NMR methodology to measure intermolecular and intramolecular KIEs at natural abundance has proven to have high precision while eliminating the arduous job of isotopically labeling starting materials.

The theoretical prediction of KIEs is often employed to distinguish among different mechanistic pathways by comparing predicted values against experimental KIEs. The KIE prediction is often performed within the framework of conventional transition state theory (TST) using the theory developed by Bigeleisen[8,9]. **Equation 1.3** allows the

theoretical prediction KIEs, where the frequencies term $(\frac{v_1^{\ddagger}}{v_2^{\ddagger}})$ represents the ratio of the stretching vibrations along the coordinate of decomposition and is an imaginary number. The term $\left(\frac{s_2}{s_1}\right)$, is the ratio of the symmetry numbers and the function $\int$ depends upon the vibrations of the molecules.

$$KIE_{TST} = \frac{v_1^{\ddagger}\left(\frac{s_2}{s_1}\right)\int GS}{v_2^{\ddagger}\left(\frac{s_2}{s_1}\right)\int TS} \qquad (\mathbf{1.3})$$

Theoretical predictions of KIEs are a semi-classical approximations and therefore do not account for contribution of tunneling into KIEs. Also, the theory of Bigeleisen and Mayer is based on conventional TST and so does not include effects associated with the more modern variational transition state theory[10] (VTS). Programs like Quiver[11] and Polyrate[12] have greatly contributed in the theoretical predictions of KIEs. Quiver,developed by Saunders and Wolfsberg, allows the prediction of KIEs from the scaled theoretical vibrational frequencies by the method of Biegeleisen and Mayer[8]. On the other hand, Polyrate allows multi-dimensional tunneling correction into KIEs as well as the predictions of KIEs taking into account VTS.

Our group has extensively combined the measurement of KIEs at natural abundance using NMR methodology with computational predictions of KIEs. Both techniques when combined have been demonstrated to be extremely powerful in discriminating between

various mechanistic proposals for chemical reactions. These techniques are our "Transition State Spectroscopy" in the elucidation of mechanisms of ordinary organic reactions.

1.2 Transition State Theory

Transition State Theory (TST) is the governing paradigm that chemists use to understand rates and selectivity in bimolecular chemical transformations. It was developed in 1935 by Eyring and Polanyi. Eyring defined a transition state as the hypersurface that divides reactants from products and passes through the saddle point of the potential energy surface.[13] TST locates the "activated complex" as the maximum in the potential energy surface. The theory utilizes the energy difference between starting materials and the activated complex in order to predict the rate of a chemical transformation. In a similar way, TST is widely used among chemist to predict the product ratio of reactions that may form more than one product. In such cases, TST is tremendously successful in accounting for chemical phenomena on both a qualitative and quantitative basis by comparing the free energy of the competing transition states. This statistical mechanical theory was developed under the assumption that the activated complex is in pre-equilibrium with reactants. The treatment of the activated complex as a molecule or compound like any other contributed to the development of a mathematical expression that describes the dependence of reaction rates with temperature. The Eyring equation as shown below, **equation 1.4**, estimates the rate of reaction (k) as a function of the

Boltzmann constant (K_B), temperature (T), Planck's constant (h), free energy of activation ($\Delta G^{\neq}$) and the gas constant (R).

$$k = \kappa \frac{(K_B\, T)}{h}\, e^{-\Delta G^{\ddagger}/RT} \qquad (\mathbf{1.4})$$

$$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\, \Delta S^{\ddagger} \qquad (\mathbf{1.5})$$

$$k = \kappa \frac{(K_B\, T)}{h}\, e^{-\Delta H^{\ddagger}/RT}\, e^{-\Delta S^{\ddagger}/R} \qquad (\mathbf{1.6})$$

By substitution of **equation 1.5** into **equation 1.4** gives the Eyring equation in terms of $\Delta H^{\neq}$and $\Delta S^{\neq}$, **equation 1.6**.

Despite the useful applications of TST to many situations in chemistry, it is a model that over simplifies reality, and as such it has its limitations. Some limitations of TST are well recognized. Theses includes the effects of transition state recrossing resulting in a decrease of the rate versus that predicted by TST, and tunneling, which increases the rate versus that predicted by TST.[13] Neglecting these variables gave rise to the inclusion of the transmission coefficient (κ) in to TST, however this correction is often ignored. Efforts to refine this original treatment of TST were made and led to the development of Variational Transition State Theory (VTS) by Truhlar and Garrett in 1980.[10] The VTST approach positions the saddle point of a chemical transformation at the maximum in Free

Energy surface to account for recrossing by minimizing the rate of reactions. There are in fact, several other ways in which TST can fail or cannot explain experimental observations in chemical reactions.

The existence of ordinary organic reactions for which TST cannot account for experimental observations have been reported as early as in 1969[14]. Later in 1984, Carpenter and Colleagues[15] studied the [1,3]-sigmatropic rearrangement of bicyclo[2.1.1]hexane-5-d and two phenyl derivatives that yielded product mixtures with retention and inversion of configuration. The different temperature dependence between the parent and phenyl analogues of bicyclo[2.1.1]hexane-5-d led Carpenter to consider different mechanistic pathways for both processes. Carpenter proposes that the [1,3]-sigmatropic rearrangement of the phenyl analogues could involve a single transition state that connected to what he described as an "intermediate", however not necessarily a minimum in potential energy, with a diradical character that could result in the formation of the experimentally observed product mixtures, **Figure 1.3**.

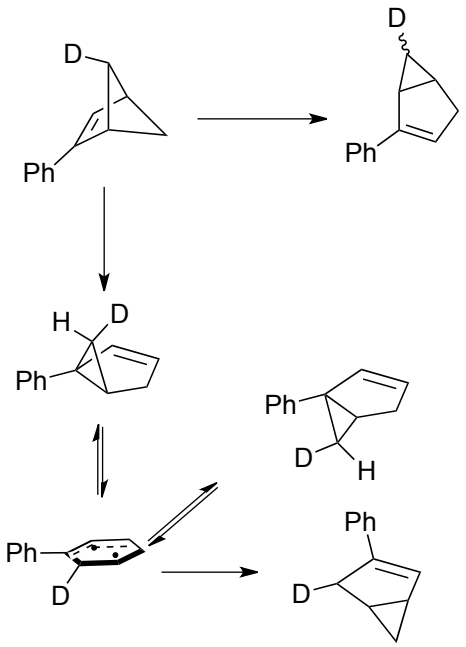

Figure 1.3 [1,3]-sigmatropic rearrangement of 2-phenylbicyclo[2.1.1]hex-2-ene-endo-5-d.[15]

Although TST could not account for Carpenter's experimental observations at the time chemistry did not count with the appropriate concepts to explain the mechanistic implications in such circumstances.

1.3 Dynamic Effects

In the quest of finding novel mechanistic ideas that can be used to explain experimental observations when TST cannot be applied, Carpenter raised the inquiry about *dynamic effects* as contributors in the selectivity of ordinary organic reactions. In 1992, Carpenter and Colleagues[16] revisited the thermal isomerization of l-phenylbicyclo[2.1.1]hex-2-ene-endo-5-d to 3-phenylbicyclo[3.1.0]hex-2-ene-6-d in a 10:1 ratio of the endo versus exo adduct, **Figure 1.4**.

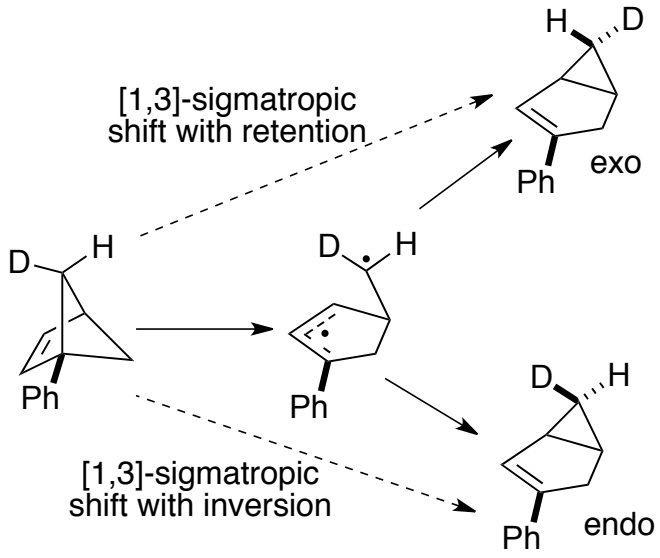

Figure 1.4 [1,3]-sigmatropic rearrangement of 1-phenylbicyclo[2.1.1]hex-2-ene-endo-5-d via a biradical "intermediate" to afford a mixture of products with inversion and retention of configuration at C-5.[16]

The unexpected 10:1 endo to exo product mixture exhibited no temperature dependence, over an 85 °C range, ruling out the possibility of competing processes. This led Carpenter to question the capability of TST to account for experimental product ratios formed in ordinary reactions. Furthermore, novel mechanistic proposals where TST and RRKM theory are not expected to work well were proposed. By studying the thermal decomposition of 2,3-diazabicyclo[2.2.1]hept-2-ene-exo,exo-5,6-d2, **Figure 1.5**, the possibility of having a potential energy surface with a single transition state and then branching into two products was introduced for the first time.

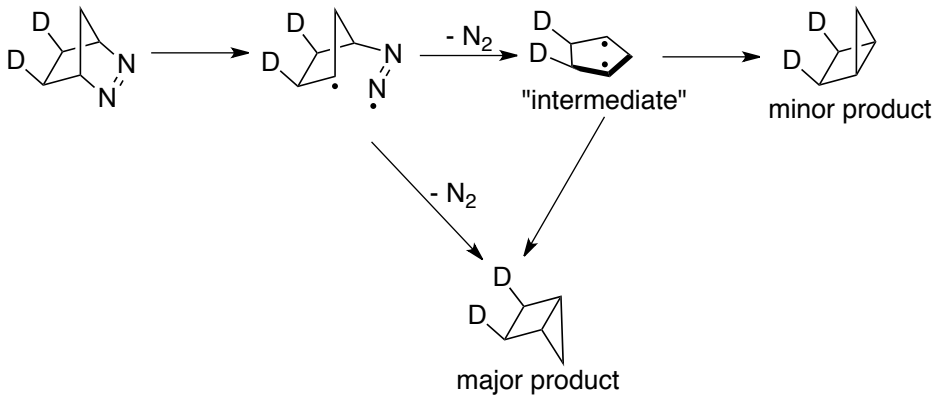

Figure 1.5 Thermal decomposition of 2,3-diazabicyclo[2.2.1]hept-2-ene-exo,exo-5,6-d2 via a "shallow" biradical intermediate.[16]

On a surface of this nature, as illustrated in **Figure 1.6**, statistical rate theories fail to explain the product ratio from a single transition state. The potential energy surface for the thermal decomposition of 2,3-diazabicyclo[2.2.1]hept-2-ene-exo,exo-5,6-d2 involves the formation of a "shallow" intermediate, however not a minimum in potential energy and therefore with excess energy, that reacts faster than it can equilibrate its internal energy to form products. Interestingly, as the 2,3-diazabicyclo[2.2.1]hept-2-ene-exo,exo-5,6-d2 losses N_2 the arrangement of the atoms on the hydrocarbon portion resembled that of the major product. The idea behind this novel mechanistic concepts are that when the simplified model that is TST fails, one must fall back on consideration of the dynamic motion and momenta of atoms.

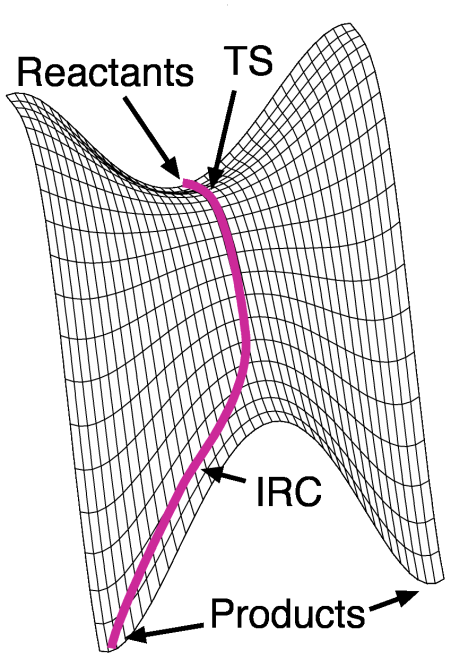

Figure 1.6 Bifurcating energy surface that connects a single transition state with a pair of products.

Dynamic Effects are experimental kinetic observations (i.e. rates, selectivity, isotope effects and formation of unexpected products) that cannot be rationalized from any of the current form of statistical rate theories. Our group has greatly contributed in identifying the influence of these novel mechanistic ideas in ordinary organic reactions. Some of the dynamic effects that have already been identified to influence in organic reactions are described below.

In *Dynamic matching*, the selectivity among pathways after passing through a shallow intermediate is influenced by the momentum of atoms at the transition state leading to the intermediate.[15-17] This form of dynamic matching has been extensively studied by carpenter since 1984 on the rearrangement of Bicyclo[2.l.l]hexene-5-d. In *Bifurcating*

energy surfaces, starting materials that cross a single transition state follow a downhill path that leads to the formation of two or more products as illustrated in **Figure 1.6**. The bifurcation of potential energy surfaces has been extensively identified, both experimentally and computationally, in ordinary organic reactions such as Diels-Alder reactions, Ene reactions[18] and ketene cycloadditons[19]. In *Incomplete intramolecular vibrational energy redistribution (IVR)* intermediates that are formed with excess energy react faster than its extra energy can equilibrate within the molecule. As a result of the formation of these "hot intermediates"[20,21], reactions like hydroboration of alkenes and ozonolysis lead to experimental product ratios that cannot be accounted for from statistical rate theories, **Figure 1.7**.

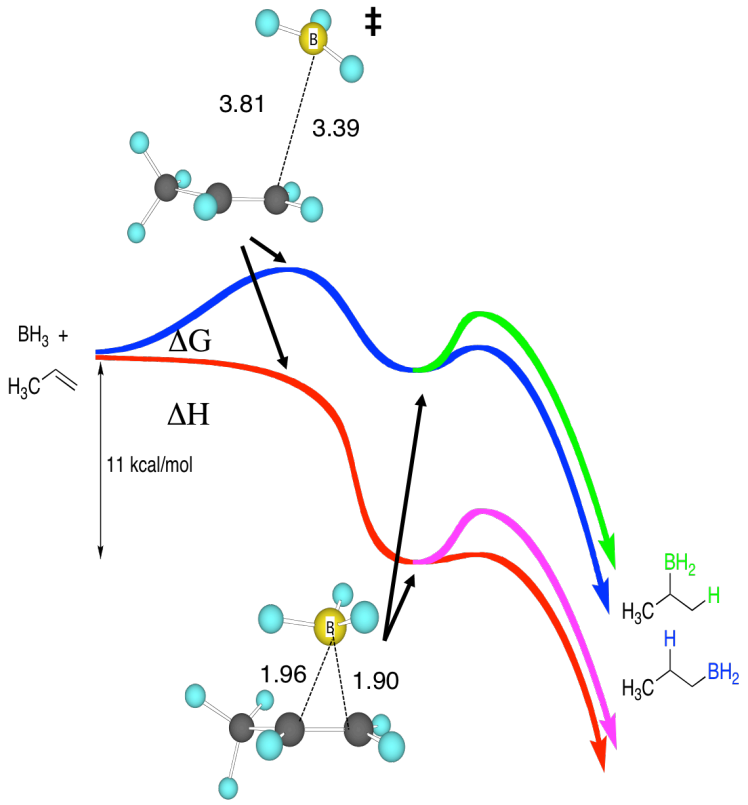

Figure 1.7 Reaction coordinate diagram for the hydroboration of alkenes. The energy profile shows that the intermediate that is formed can surmount, both barriers makonikov and anti-makovnikov, due to its excess energy.[20]

In *Entropic bifurcation*, an enthalpically downhill path competes against an entropically uphill path leading to the formation of unexpected products. **Figure 1.8** illustrates the entropic bifurcation on the Free energy surface for the [2,3] sigmatropic rearrangement of ammonium ylides.[22]

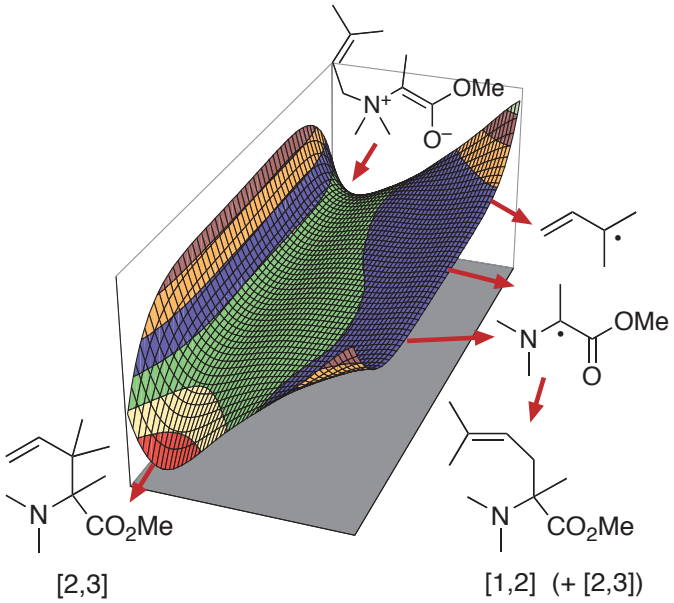

Figure 1.8 Entropic bifurcation on the free energy surface for the [2,3] sigmatropic rearrangement of ammonium ylides leads to the formation of the [2,3] allowed and [1,2] forbidden products from the same transition state.[22]

In *Non-statistical recrossing*, molecules that pass over an initial transition state run into an imaginary "wall" and recross the transition state to go back to starting materials.[23] In Newtonian Isotope Effects, lighter isotopes accelerate faster than heavy isotopes when exposed under a constant force; **F = m x a**. Our group first reported this novel form of isotopes effects on the dimerization of cyclopentadiene.[24] The atomic motion shown on **Figure 1.9**, illustrates the motion taken by the each isotopomers (^{12}C and ^{13}C) on the dimerization of methacrolein leading to the product formed by greater motion of the lighter isotope, ^{12}C.[25]

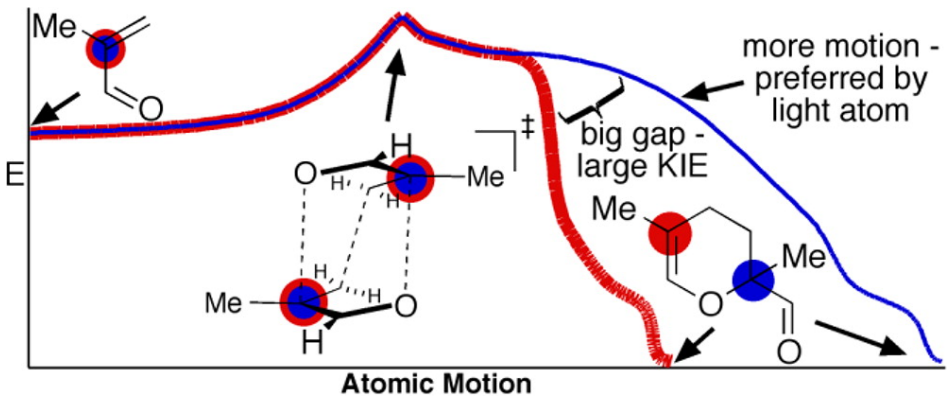

Figure 1.9 Atomic motion reaction coordinate diagram for showing the motion of ^{12}C versus ^{13}C on the thermal dimerization of methacrolein.[25]

CHAPTER II

STRUCTURAL EFFECTS IN NEWTONIAN KINETIC ISOTOPE EFFECTS*

2.1 Introduction

Ordinary KIEs originate mainly in the quantum effects of zero-point energy (ZPE) and tunneling. In contrast, Newtonian KIEs appear to result simply from the greater acceleration of lighter masses in response to a force (i.e., **F** =**ma** ,Newton's second law). In 2009, our group reported the first example of this novel form of kinetic isotope effects by studying the dimerization of cyclopentadiene.[24] Computational studies have shown that the lowest energy transition state structure for this reaction is C_2 symmetrical and has two sets of [4+2] orbital interactions, also referred as a bispericyclic structure as reported by Caramella & co-workers.[26] This reaction can lead to the formation of a pair of products that are chemically equivalent, but isotopomerically distinguishable. The ratio of the isotopologue products constitutes an intramolecular KIE and reflects the selectivity of the reaction to favor the formation of one isotopologue.

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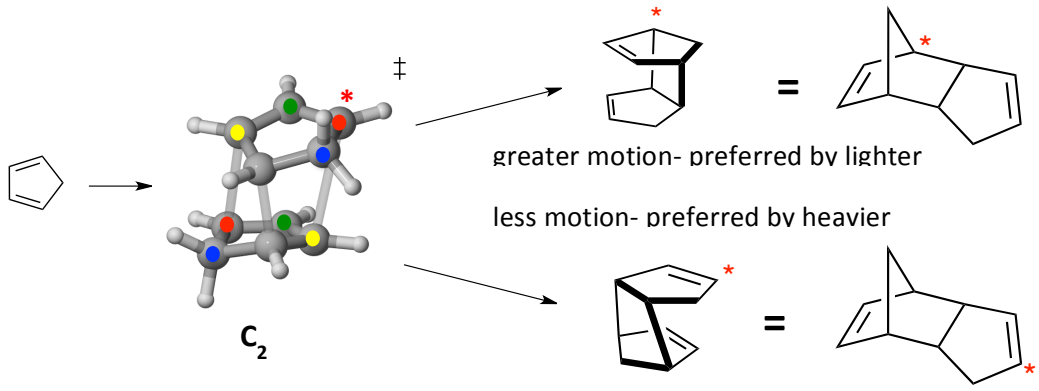


Figure 2.1 Cyclopentadiene dimerization via a C_2 symmetrical transition state structure that leads to the formation of two isotopomeric products. The labeled carbon represents a ^{13}C label at a particular position in one of the cyclopentadiene molecules.[24]

Interestingly, when intramolecular KIEs were measured for a sample of dicyclopentadiene, unusual isotope effects that could not be understood from TST were observed. These experimental isotope effects reflected a preference for the formation of the isotopomeric cyclopentadiene dimer that contains a greater amount of ^{12}C at the newly formed sigma bonds. An experimental product selectivity between two isotopomeric products provided experimental evidence that suggested a bifurcation on the potential energy surface of this reaction. The bifurcation in the potential energy surface connects a single transition state structure with a pair of isotopologues of dicyclopentadiene, as illustrated in **Figure 2.1**. In light with the results obtained from the cyclopentadiene dimerization, isotope effects in chemical reactions could be originated not exclusively from quantum mechanical phenomena but also from classical physics. As a result of the above mention scenario regarding the origin of isotope effects, the identification of Newtonian KIEs in other chemical reactions is crucial for its understanding.

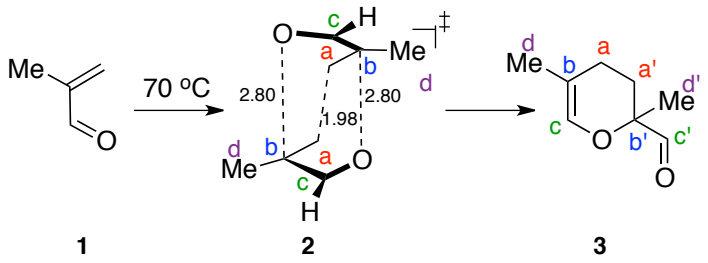


Figure 2.2 Thermal dimerization of methacrolein.

We describe here a system, in the thermal dimerization of methacrolein, where dynamic effects, Newtonian Isotope Effects and Non-Statistical Recrossing, impact on the product selectivity. The interest behind studying this ordinary hetero Diels-Alder reaction arises from the desire in elucidating the origin of these unusual KIEs, (Newtonian KIEs), and determine which of the above mentioned dynamic effects is controlling the selectivity of the reaction.

Each ^{13}C-containing molecule of methacrolein can lead to the formation of two isotopomeric cycloadducts, and their ratio constitutes an intramolecular KIE that reflects the selectivity among trajectory outcomes on the *bifurcating energy surface* of the reaction. As illustrated on **Figure 2.2**, a C_2 symmetrical transition state structure breaks its symmetry to afford products of lower symmetry. The experimentally measured intramolecular kinetic isotope effects are discussed along this chapter. In addition, a standard computational study including location of stationary points along the potential energy surface for this reaction in combination with molecular dynamics were employed to compare computational predictions and experimental data.

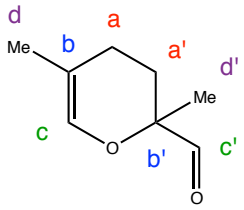
2.2 Experimental Results

Dimerization of Methacrolein. A sample of 5.00 mL (4.24 g, 60.4 mmol) of methacrolein (dimer-free) and a crystal of hydroquinone was heated at 70 °C for 7 d. The mixture was then distilled by vacuum transfer from -78 °C to 25 °C to afford 1.24 g (29.5 %) of 2,5-dimethyl-3,4-dihydro-2H-pyran-2-carbaldehyde as a light yellow oil with no observable impurities by ^{1}H and ^{13}C NMR. The spectral properties matched those previously reported.[27] A closely analogous procedure was used to obtain an additional sample of the dimer for analysis.

Experimental Kinetic Isotope Effects. NMR samples were prepared using between 260 mg and 270 mg of methacrolein dimer in 5 mm NMR tubes filled to a constant height of 5 cm with $CDCl_3$. The ^{13}C spectra were recorded at 125.81 MHz using inverse gated decoupling, delays of 26 s for a/a', 276 s for b/b', 57 s for c/c' and 15 s for d/d' between $\pi/2$ calibrated pulses and a 15 s acquisition time to collect 961,540 points. Integrations were numerically determined using a constant integration region for each peak that was a constant multiple of the peak widths at half-height. In accordance with the methodology we have previously published, for the integration of each pair of corresponding positions within the methacrolein dimer the transmitter was set half way in between the two peaks of interest on each measurement[5]. A zero-order baseline correction was generally applied, but to avoid any qualitative manipulation no first-order or higher-order baseline correction was ever applied. Six spectra were recorded for each pair of positions on each sample. The assignments of the peaks in the ^{13}C spectrum of methacrolein dimer was

consistent with 2D-NMR (INADEQUATE, COLOC) experiments reported in the literature[27].

The experimental intramolecular KIEs for the thermal dimerization of methacrolein were measured for two independently prepared samples of methacrolein dimer at 70 °C. The experimental intramolecular KIEs are summarized in **Figure 2.3**, and they show a preference to have a greater amount of ^{12}C at the newly formed sigma bonds, similar to what has been previously observed for the dimerization of cyclopentadiene[24].



	Relative Amount of ^{13}C (x'/x)	KIE
a	**0.989(2)**	**1.011(2)**
b	**0.981(2)**	**1.019(2)**
c	**1.006(1)**	**0.994(1)**
d	**1.001(1)**	**0.999(1)**

Figure 2.3 Experimental intramolecular Kinetic Isotope Effects for methacrolein dimer. KIEs were measured at natural abundance in $CDCl_3$

Although we hypothesize that the nature of these KIEs could in principle be classical physics as in the cyclopentadiene dimerization, in order to test our hypothesis we need to turn into computational studies. The results obtained from these calculations are presented and explained in the following sections.

2.3 Computational Results

Choosing the Optimal Method and Basis Set. The selection of the most accurate method for the study of the potential energy surface for this system is essential. In order to obtain results that are meaningful and can be compared against experimental results, the relative position of all stationary points along the reaction's energy surface was taken into consideration. In the thermal dimerization of methacrolein, two minima and two maxima were identified along the reaction surface. The two minima correspond to the starting materials and product, and the two maxima correspond to the conventional transition state and the [3,3]-Cope rearrangement transition state structure that interconverts the pair of isotopomeric products as shown in **Figure 2.4**. All transition states have only one imaginary frequency.

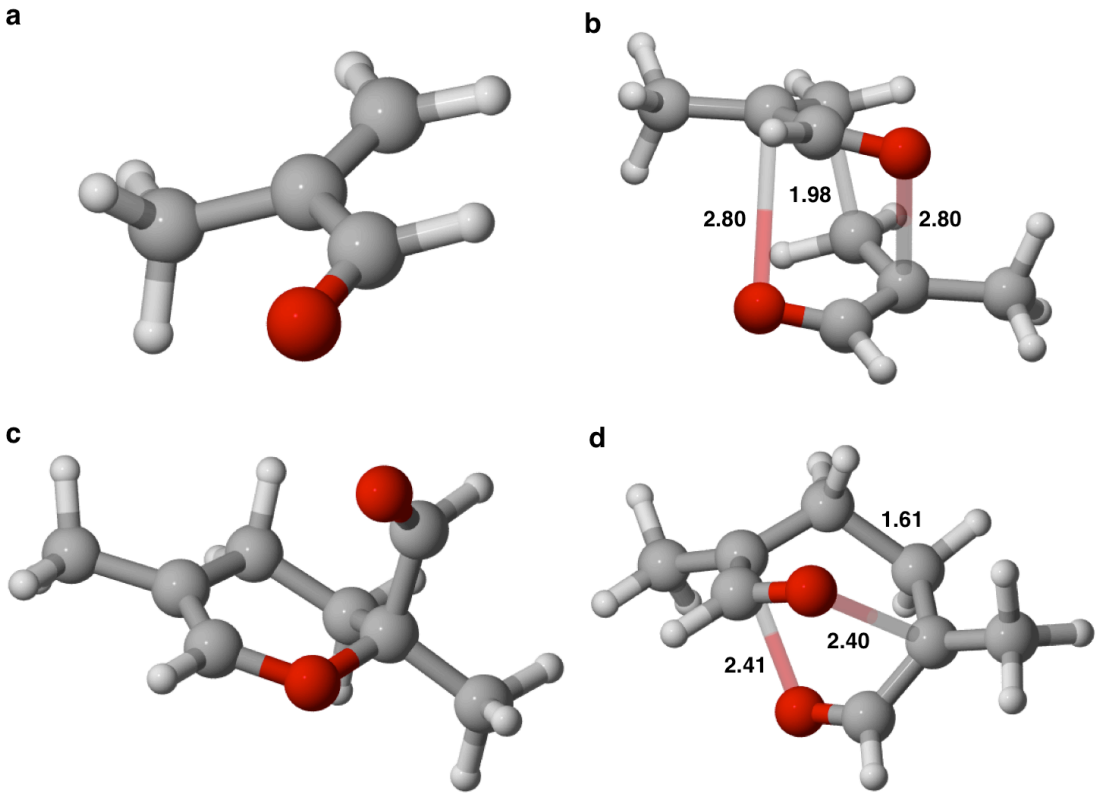


Figure 2.4 Stationary points located on the energy surface for methacrolein dimerization using B3PW91/6-31G* in the gas phase. a. Optimized structure of methacrolein. b. Transition state structure for the dimerization of methacrolein showing the two sets of [4+2] orbital interactions. c. Optimized structure of methacrolein dimer. d. Transition state structure for the [3,3]-Cope rearrangement that interconverts from one isotopologue to the other.

In choosing of the methodology employed in the dynamic calculation, the goal was to find an accurate DFT method with a reasonable basis set that would most accurately depict the shape of the energy surface in the area around and beyond the Diels-Alder transition state. B3PW91 was chosen because its relative energies most closely resemble those obtained from high-level calculations such as G3B3 and G4. **Table 2.1**

summarizes the free energies and enthalpies obtained from different methods using the Diels-Alder cycloaddition transition state as the zero of energy.

Table 2.1 Relative free energies and enthalpies for the starting material, Cope transition state and products using the Diels-Alder transition state as the zero of energy.

Structure	Method/basis set	Enthalpy, kcal/mol	Free Energy, kcal/mol
SM	G4	-18.1	-32.1
COPE TS		-3.8	-2.0
Product		-39.5	-38.7
SM	G3B3	-17.8	-31.8
COPE TS		-3.6	-1.9
Product		-39.5	-38.7
SM	B3LYP/6-31G*	-19.6	-33.6
COPE TS		-2.1	-0.4
Product		-33.1	-31.9
SM	B3LYP/6-31+G**	-22.7	-36.7
COPE TS		-1.8	-0.1
Product		-31.8	-30.5
SM	MP2/6-31+G**	-10.4	-24.6
COPE TS		5.7	9.2
Product		-32.1	-30.6
SM	M06/6-31G*	-12.1	-25.6
COPE TS		-2.4	-0.2
Product		-36.1	-34.2
SM	M06/6-31+G**	-14.5	-27.5
COPE TS		-2.3	0.3
Product		-34.8	-32.3

Table 2.1 Continued

Structure	Method/basis set	Enthalpy, kcal/mol	Free Energy, kcal/mol
SM	M06-2X/6-31+G**	-16.6	-32.0
COPE TS		0.4	0.7
Product		-41.2	-41.2
SM	MPW1K/6-31+G**	-21.4	-35.5
COPE TS		-3.6	-1.6
Product		-48.8	-47.6
SM	O3LYP/6-31+g**	-25.6	-38.8
COPE TS		-2.4	0.0
Product		-32.6	-30.5
SM	BP86/6-31+g**	-14.9	-28.4
COPE TS		-4.7	-2.4
Product		-27.1	-25.4
SM	BB1K/6-31+g**	-20.8	-35.1
COPE TS		-3.0	-1.2
Product		-42.6	-41.4
SM	BP86/6-31g*	-12.4	-26.2
COPE TS		-5.1	-3.0
Product		-28.4	-26.9
SM	B3PW91/6-31+G**	-19.9	-33.6
COPE TS		-3.8	-1.6
Product		-36.0	-34.4
SM	B3PW91/6-31G**	-17.7	-31.8
COPE TS		-4.0	-2.1
Product		-36.9	-35.6

Table 2.1 Continued

Structure	Method/basis set	Enthalpy, kcal/mol	Free Energy, kcal/mol
SM	B3PW91/6-31G*	-17.6	-31.6
COPE TS		-4.1	-2.1
Product		-37.2	-35.8
SM	B3PW91/6-31+G*	-11.7	-24.8
COPE TS		-5.3	-2.5
Product		-27.9	-25.8

Steepest-Descent Path in Mass Weighted Coordinate. Intrinsic Reaction Coordinate (IRC) calculations are known to follow the minimum energy pathway on the potential energy surface of a reaction. These calculations start from a transition state geometry and follow a steepest-descent in mass weighted coordinate path towards products or starting materials.

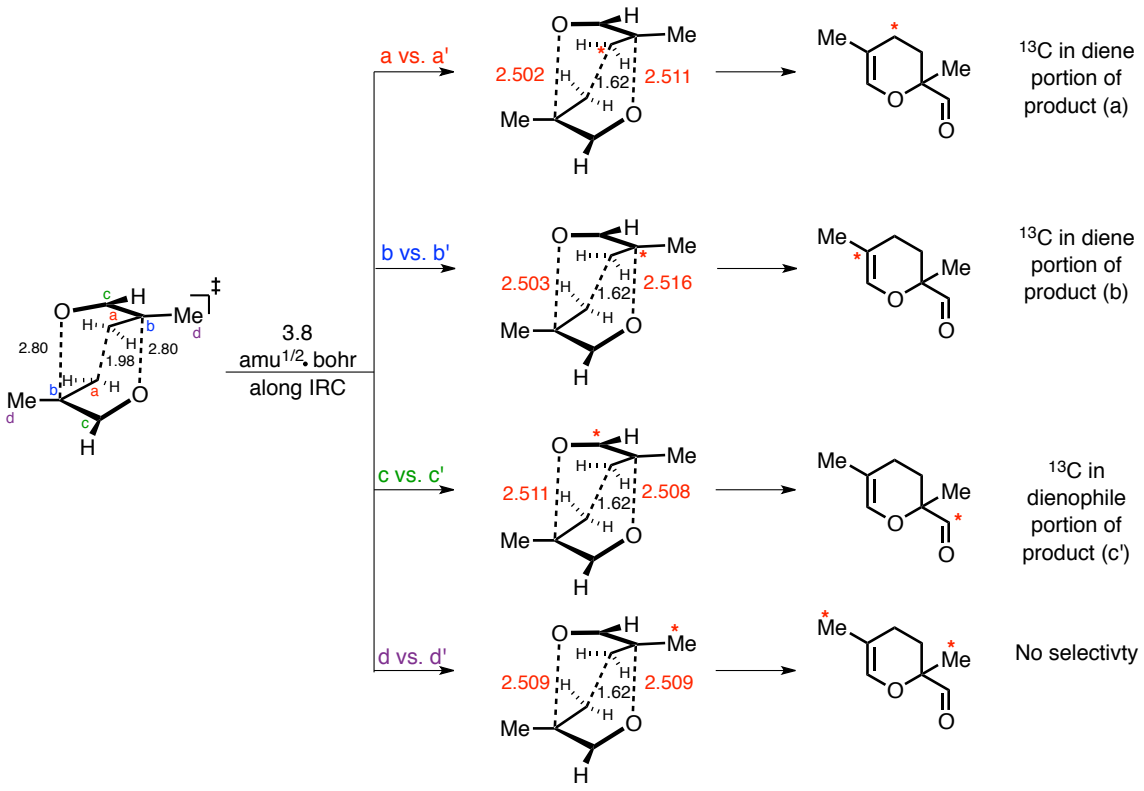


Figure 2.5 Structures on the IRCs after the cycloaddition transition state with ^{13}C substitution, showing the desymmetrization toward the major product.

Since there is only one minimum energy pathway in the potential energy surface of a reaction, when initializing IRC calculations from the transition structure for the methacrolein cycloaddition reaction with an isotopic label (^{13}C) at one of the methacrolein moieties will connect to only one of the dimeric isotopologues. IRCs were followed forward from the cycloaddition transition state in B3PW91/6-31+G** calculations (chosen because they fit best here with high-level ab initio methods; see **Table 2.1**), with a ^{13}C placed in position **a** , **b** , **c** , or **d** (**Figure 2.5**). For positions **a** and **b** of the transition structure, the IRC is desymmetrized toward placing the ^{13}C in the diene portion of the dimer (positions **a** and **b** as opposed to **a'** and **b'**), while a ^{13}C in

position **c** of the transition structure ends up in the dienophile portion (position c'). The desymmetrization of the IRC correctly predicts the major product on each case and the extent of desymmetrization corresponds strikingly well with the magnitude of the experimental isotope effect. For position d, the IRC follows a nearly symmetrical path for a long distance from the transition state region before falling to position d in the dimer and no significant selectivity is observed in accordance with experimental observations.

Exploration of the Variational Transition State Theory Apporach. Following Lluch's procedure[28], the valley-ridge inflection Point (VRI) region was located on the B3PW91/6-31+G** surface. This was achieved by following the steepest descent in mass weighted from the cycloaddition transition state until an orthogonal desymmetrizing mode (the morphed mode #2) had approximately zero curvature. This initial path was obtained with ^{12}C / ^{1}H in all positions. The VRI geometry obtained is given in a later section. For the VRI, new frequency calculations were carried out with isotopic substitution, and the remainder of the discussion will refer to the most-carefully explored case where a ^{13}C was placed in carbon **a**. From the VRI, a 0.05 Å step was taken along the zero-curvature mode in each direction to obtain two new points that were used as the starting points for new steepest-descent paths in mass weighted coordinates (including the ^{13}C in carbon **a**). The complete paths obtained, consisting of approximately 650 structures each. Frequency calculations were carried out at 20-point intervals along these paths. For one of these paths, a plot of the free energies calculated

by Gaussian09, based on frequencies in Cartesian coordinates, is given below on **Figure 2.6**.

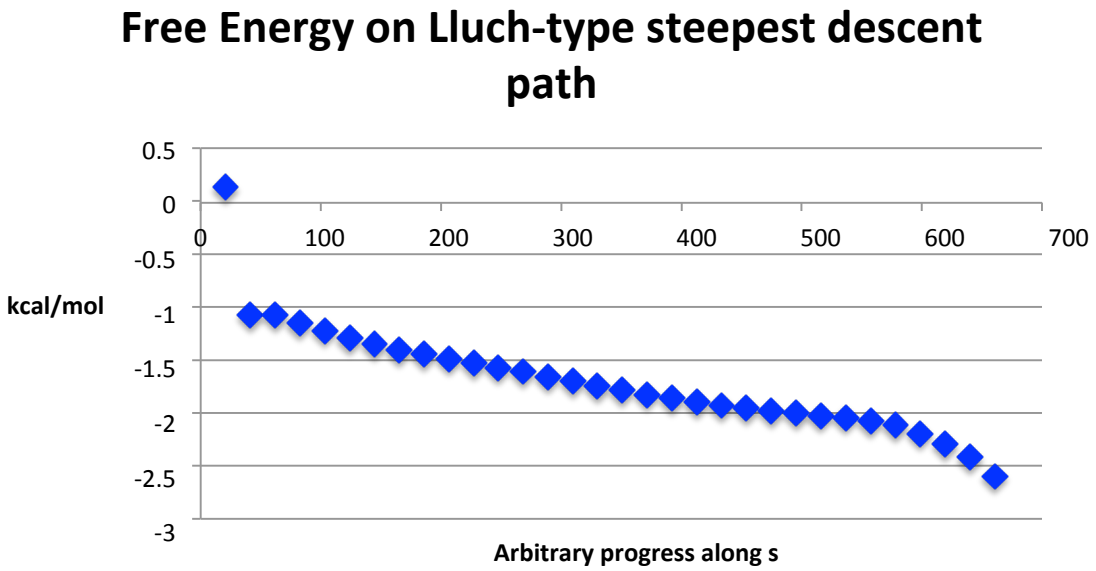


Figure 2.6 Plot of the harmonic free-energy estimate for points along the Lluch-type steepest descent path on B3PW91/6-31+G**. The zero of free energy was set as the cycloaddition transition state structure.

One discontinuity is obvious – at the beginning as the path passes from an area containing one imaginary frequency. Such discontinuities are not real bottlenecks, and the remainder of the free-energy path is monotonically downhill.

Dynamic Trajectories. Direct dynamic trajectories were employed to gain quantitative insight into the experimental KIEs. In order to over come the difficulty (time and computational cost) of running dynamic trajectories with a ^{13}C in one of the methacrolein moieties we took advantage of our trick of starting dynamic trajectories

with *in silico*, superheavy carbon atoms. Quasi-classical dynamic trajectories in the gas phase, on a B3PW91/6-31G* energy surface were initialized from isotopomers of the cycloaddition transition state structure, containing a single ^{16}C, ^{20}C, ^{28}C, ^{44}C, ^{76}C, or $^{140}C(12+2^{N}$ amu, **N** =2, 3,4, 5, 6, or 7). Each normal mode in the transition state structure was give its zero point energy (zpe), along with a Boltzman distribution of a sample at 70 °C, with a random phase. Because the lowest-energy real normal mode in the cycloaddition transition state structure, "mode 2" desymmetrizes the structure in a way that has a large effect on trajectory outcomes, an equal number of trajectories were given positive versus negative velocities in this mode. The transition vector was given a Boltzmann sampling of energy 'forward' from the col. The trajectories were integrated until either the product was formed (median time 90 fs) or the starting materials were reformed and the results are summarized in **Table 2.2**.

Table 2.2 Quasi-classical dynamic trajectories initialized from the cycloaddition transition state structure on a B3PW91/6-31G* energy surface.

Position / mass	Total Runs	Total x	Total x'	Recrossed	KIE
a/a' 140	8168	4227	3366	575	1.26 ± 0.05
a/a' 76	2530	1274	1083	173	1.18 ± 0.07
a/a' 44	2604	1279	1111	214	1.15 ± 0.06
a/a' 28	4066	1980	1763	323	1.12 ± 0.05
a/a' 20	5688	2652	2499	537	1.06 ± 0.04
			extrapolated to ^{13}C 1.013		
b/b' 140	9312	4965	3300	1047	1.50 ±0.05
b/b' 76	3082	1588	1150	344	1.38 ± 0.09
b/b' 44	3050	1532	1194	324	1.28 ± 0.07
b/b' 28	7824	3773	3290	761	1.15 ± 0.04
b/b' 20	14828	6916	6404	1508	1.08 ± 0.03
b/b' 16	20932	9690	9149	2093	1.06 ± 0.02
			extrapolated to ^{13}C 1.017		
c/c' 140	3214	1383	1471	360	0.94 ± 0.05
c/c' 76	3074	1346	1390	338	0.97 ± 0.06
c/c' 44	7848	3418	3579	851	0.96 ± 0.04
d/d' 140	3666	1580	1701	385	0.93 ± 0.06
d/d' 76	6512	2904	2890	718	1.00 ± 0.04

Dynamic trajectories correctly predict the major product in each case, and the magnitude of the selectivity in the trajectories follows the same trend as in the experimental KIEs. As the mass of the "super heavy" carbon atoms is increased the selectivity of the reaction is also increased in all positions. Trajectories with a label on position d exhibit a small selectivity with a heavy carbon of mass 140 amu, but with ^{76}C no selectivity was observed. This observation is consistent with a concerted but asynchronous transition state, where both C-C and C-O bonds are progressing in formation. If full C-C bond forming occurs without any C-O bond formation, the transition state structure would have a full diradical caracter, **Figure 2.7 a**, and the radicals would be stabilized by the

methyl groups. In this reaction the transition state structure never actually takes a full diradical character, but it is still stabilized by the methyl groups that donate into the low-lying σ* orbitals associated with the also forming C-O bond, **Figure 2.7**. As a result of this, the energy surface in the area past cycloaddition transition state is more downwardly sloped with the methyl groups present than absent, and in the absence of any statistical dynamical bottleneck the more highly sloped surface resists recrossing. With minimal recrossing in the methacrolein cycloaddition, the Newtonian preference dominates the selectivity of the reaction.

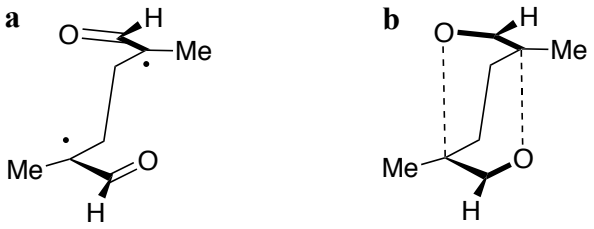


Figure 2.7 a. Methyl groups stabilize the diradical character of the intermediate formed from a stepwise reaction. b. Methyl groups stabilize the structure by donating into the C-O σ* orbitals.

Results from quasi-classical dynamic trajectories show an increment of the isotope effects that is directly proportional to the mass of the "superheavy" carbon atoms. In order to elucidate whether this trend arises from ZPE as it is true for normal isotope effects, a second set of classical dynamic trajectories were initialized, **Table 2.3**. On these trajectories ZPE was turned off, giving each normal mode a classical distribution of energy.

Table 2.3 Classical dynamic trajectories initialized from the cycloaddition transition state structure on a B3PW91/6-31G* energy surface.

Position / mass	Total Runs	Total x	Total x'	Recrossed	KIE
a/a' 140	3626	1908	1503	215	1.27 ± 0.06
a/a' 76	2340	1187	996	157	1.19 ± 0.07
a/a' 44	3494	1741	1512	241	1.15 ± 0.05
a/a' 28	3880	1887	1734	259	1.09 ± 0.05
a/a' 20	4012	1949	1793	270	1.09 ± 0.05
b/b' 140	3640	2040	1303	297	1.57 ± 0.07
b/b' 76	3430	1844	1339	247	1.38 ± 0.07
b/b' 44	4298	2172	1812	314	1.20 ± 0.05
b/b' 28	2812	1403	1224	185	1.15 ± 0.07
b/b' 20	7992	3850	3567	575	1.08 ± 0.03
c/c' 140	4186	1816	2026	344	0.90 ± 0.04
c/c' 76	6380	2803	3082	495	0.91 ± 0.03
c/c' 44	12588	5813	5862	913	0.99 ± 0.03

These results are statistically indistinguishable from those in **Table 2.2**, so quantum mechanical ZPE did not change the dynamics. Since a fully classical simulation accounts for the KIEs, they do not arise from any quantum-mechanical effect and hence the KIEs are Newtonian in origin.

To calculate the uncertainties in the trajectory ratios, we set up an Excel spreadsheet that would repeatedly simulate the complete set of trajectory runs with each choice of superheavy carbon. In the simulations, the outcome of each individual trajectory depended on a random number and on a weighting that corresponded to the ratio of outcomes actually observed in the set of trajectories. Because of the weighting, the average outcome of an infinite number of Excel simulations would be equal to the

outcome observed in the trajectories. Each individual simulation, however, departs from the observed outcome in a way that reflects the role of random chance on the results in a set of trajectories. From the results of 119 simulations, standard deviations was calculated: mass-140: 0.018; mass 76 0.022; mass 44 0.025; mass 28 0.018. The 95% confidence ranges would be twice these standard deviations. (A common mistake in handling experimental data is to set the 95% confidence range to twice the standard deviation, but in this case, because of the nature of the simulation, it is actually correct.)

Extrapolation of Trajectory Results to ^{13}C. The process for extrapolation of the trajectory results to ^{13}C starts with the assumption that the additional isotope effect per additional mass unit decreases as the mass grows. For example, the effect of going from ^{13}C to ^{14}C would be larger than the effect of going from ^{140}C to ^{141}C. We further assumed that this decrease with mass is nonlinear with a decreasing slope, that is, that a plot of the additional isotope effect per additional mass versus mass would have a greater slope at low masses (e.g., ^{13}C to ^{14}C) than at high masses (e.g. ^{140}C to ^{141}C). These simple assumptions exclude some extrapolation processes that would lead to physically unreasonable isotope effects at both high masses and at ^{13}C.

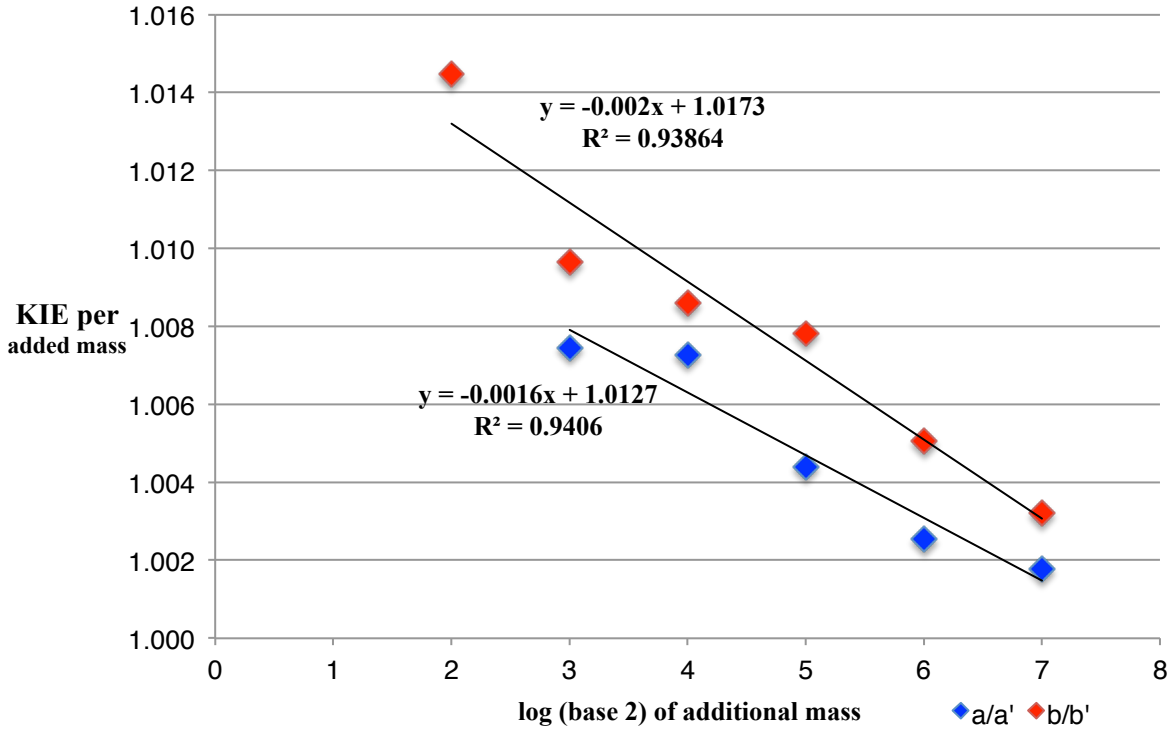


Figure 2.8 Extrapolated ^{13}C KIEs for **a/a'** anb **b/b'** from quasi-classical dynamic trajectories on Table 2.2.

Table 2.2 and the associated graph **(Figure 2.8)** show the data used in the extrapolation, the extrapolated results, and the complete linear regression analysis and statistics. The Nominal KIEs come from the **Table 2.2** on the previous section. The "additional mass" is defined as the mass beyond 12 amu. The "isotope effect per mass" is defined as the geometric average (**equation 2.1**).

$$\text{isotope effect per mass} = (\text{Nominal KIE})^{(1/(\text{additional mass}))} \quad \textbf{(2.1)}$$

The extrapolation was then carried out by assuming a linear relationship between the log of the additional mass (the base is arbitrary but set conveniently here as 2) versus the isotope effect per mass.

The extrapolation process used the Regression tool in Microsoft Excel 2011 for Mac, Version 14.3.9.

Atomic Motion Reaction Coordinate Diagrams. The IRC and dynamic results are each impressively predictive, however they are not explanatory. With the purpose of providing insight into both the direction of the isotope effects and their magnitude, we introduce atomic motion reaction coordinate diagrams (**Figure 2.9**). These diagrams are easily generated by plotting the distance that each atom has moved with respect to the previous point against the energy of each structure (At each point in an IRC the distance that each atom moved versus the previous point, with a fixed center of mass and rotational orientation, is calculated and the sum of these distances up to that point is plotted versus the energy).

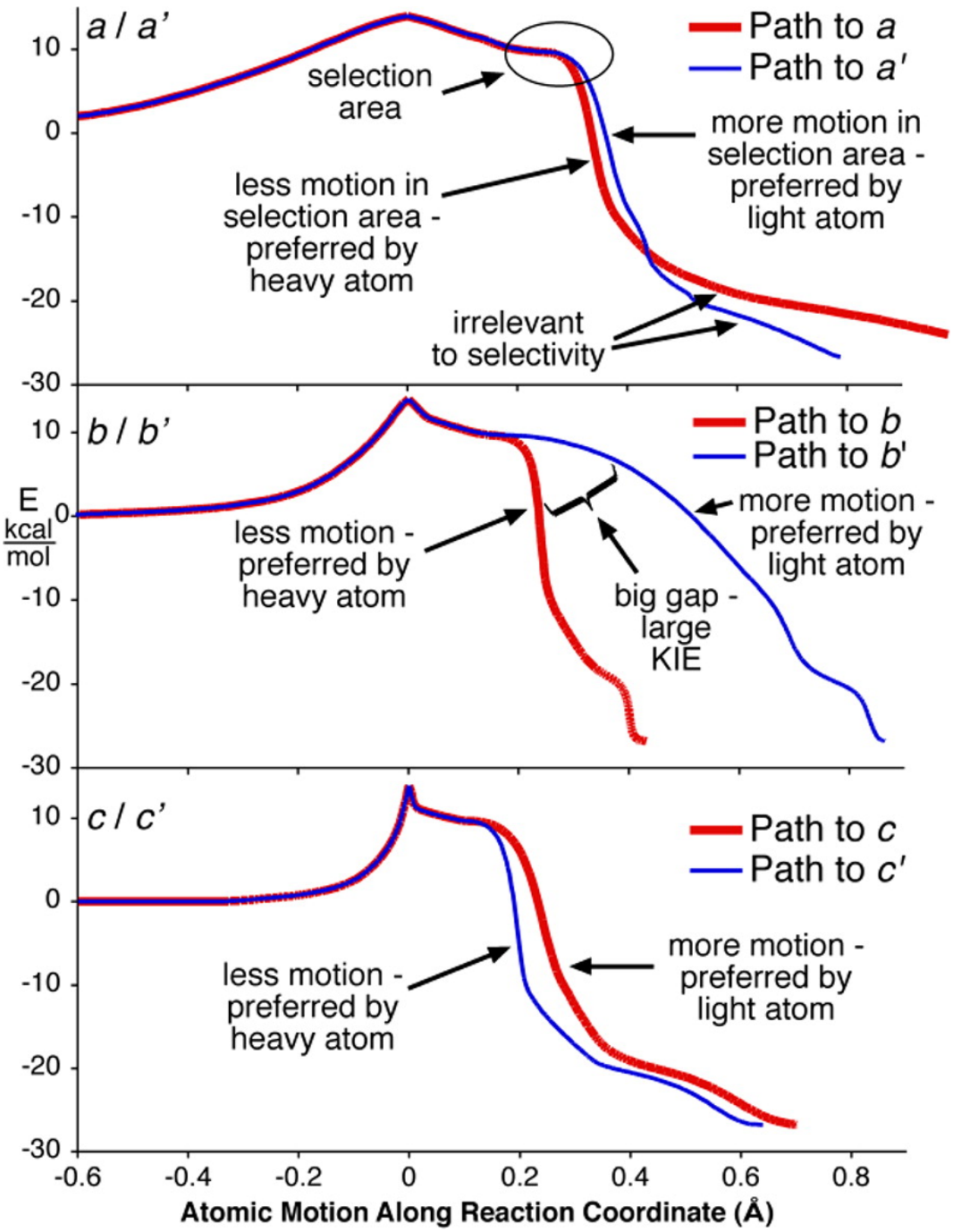


Figure 2.9 Atomic motion reaction coordinate diagrams.

There are two striking observations in the diagrams. The first is that the major product is not defined by what position moves the lightest atom the farthest in going from the TS to the product geometry. This can be seen for the **a /a'** diagram; the path to position a in the product ultimately requires greater atom motion, yet the heavier isotope preferentially goes to this position. The direction of the isotope effect is instead determined by the relative atomic motion in the small area of the reaction coordinate diagram where the paths initially separate. After this point, the product has already been decided and the atomic motion becomes irrelevant to the reaction selectivity. In each case the preferred product moves the lighter atom, ^{13}C, farther in the "selection area." The second observation is that the largest KIE, that for the **b /b'** pair, is associated with a large gap between the paths taken by the racing pairs of isotopes (^{12}C vs. ^{13}C). The C-O bond formation that consummates product formation requires extensive motion on the part of the carbon atom forming this bond, and as a result the lighter isotope is strongly preferred for this position.

2.4 Discussion

The existence of KIEs for this reaction is extremely surprising since the products that are formed from this reaction are isotopologues, and therefore chemically equivalent products that are formed from a single transition state. The lowest energy transition state structure located using several methods and that will be discussed in more detail on a later section, has C_2 symmetry and therefore both aldehyde molecules are equivalent at the transition state region. Given this, one might wonder where is selectivity in

methacrolein dimerization reaction arising from? Further more, what is the nature of these unusual KIEs. The fact that there are any KIEs on the thermal dimerization of methacrolein, strongly suggests the existence of a bifurcation in the potential energy surface for this reaction and this idea is supported by identifying the VRI region that leads to a two orthogonal pathways corresponding to the pair of isotopologue cycloadducts. One of the products has more ^{12}C at the newly formed sigma bonds, this is the experimentally observed major product, and the other product contains more ^{13}C at the newly formed sigma bonds and it is experimentally observed as a minor product from this reaction. As a result of having a bifurcating energy surface, and in the absence of a dynamical bottleneck, TST cannot account for the experimental selectivity in the hetero Diels-Alder reaction of methacrolein with itself. Quasi-classical dynamic trajectories accurately predict the experimental product ratio. In addition, second sets of dynamics, classical dynamics (no ZPE), were initialized no significant change in the KIEs was observed. This observation supports our initial hypothesis that these isotope effects originate from classical phenomena, Newton's second Law, and minimal amount of recrossing does not control the selectivity in the reaction (recrossing would play against Newtonian KIEs). Atomic motion reaction coordinate diagrams qualitatively describe the mechanistic picture for this cycloaddition.

While in most reactions, isotopic selectivity or any other form of product selectivity would be simply understandable from the free energies of TSs. Here, the story is more complex

and more interesting. The race between carbon atoms to positions in the product is not decided by TS energies, and it is not decided by the dynamic effect of recrossing in this case. Rather, the selectivity is decided by forward motion in the small area of the energy surface that selects the product. Even so, dynamic matching predecides most races, but a substantial number are won by the greater motion of lighter atoms. The ideas here are all quite qualitative, but they appear useful for insight into experimental observations in the growing list of reactions known to involve dynamic effects.

CHAPTER III

TEMPERATURE DEPENDENCE IN NEWTONIAN KINETIC ISOTOPE EFFECTS

3.1 Introduction

Isotopic fractionation originates from the difference in vibrational frequencies between isotopes.[2] The potential energy wells for all species on an energy surface are composed of multiple vibrational states. Consequently, temperature can impact isotopic fractionation as a result of the change in the population of vibrational states at different temperatures. Our group has identified two examples of Diels-Alder reactions that lead to experimental Isotope Effects that do not originate from any quantum mechanical phenomena like ZPE or tunneling. We refer to these isotope effects as Newtonian KIEs as their origin is believed to arise from the difference in mass between isotopes, a purely classical phenomenon. These examples have been of great interest because they could lead to the design of new physical experiments to shed light about the origin of this novel Isotope Effects. As discussed on the previous chapter, quasi-classical dynamic trajectories can accurately predict the experimental KIEs for previously studied systems. Interestingly when classical dynamic trajectories were initialized the results obtained were indistinguishable from those obtained from quasi-classical dynamic trajectories. From this observation computational studies have suggested that these isotope effects have a negligible or no contribution from ZPE.

The contribution of ZPE into KIEs arises from the difference in vibrational frequencies of molecules containing different isotopes of an element. We sought to find experimental evidence that is in agreement with theoretical predictions about the origin of Newtonian Isotope Effects. For such purpose, we have turned our interest in the study of the dimerization of cyclopentadienone for two main reasons, **Figure 3.1**.

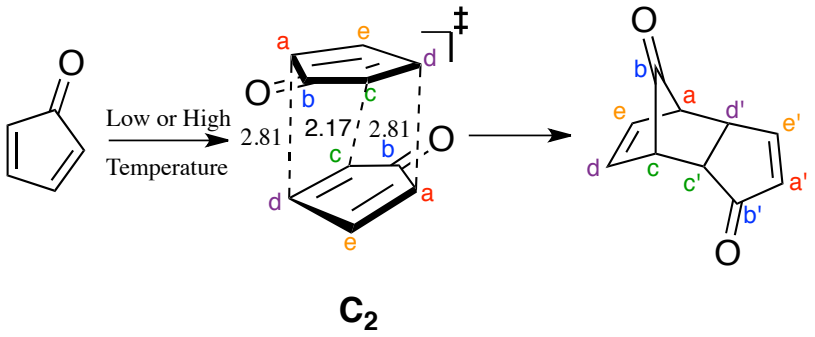


Figure 3.1 Dimerization of cyclopentadienone via a symmetric bispericyclic transition state structure to afford an unsymmetrical dimer as product.

First, the lowest energy transition state structure for the dimerization of cyclopentadienone is known to have two sets of [4+2] orbital interactions[29], also known as a bispericyclic transition structure, making this Diels-Alder reaction a possible candidate to exhibit Newtonian KIEs. Second, the dimerization of cyclopentadienone makes an ideal system to study under a broad range of temperatures. As a result of the negligible contribution of ZPE into Newtonian KIEs on the cyclopentadienone dimerization reaction we hypothesize that isotope effects measured at different temperatures will be indistinguishable from each other. With the purpose of learning gaining knowledge about the temperature effect on the experimental KIEs for

cyclopentadienone dimerization we will study this reaction at a low and high temperature in order to measure intramolecular KIEs of the dimer.

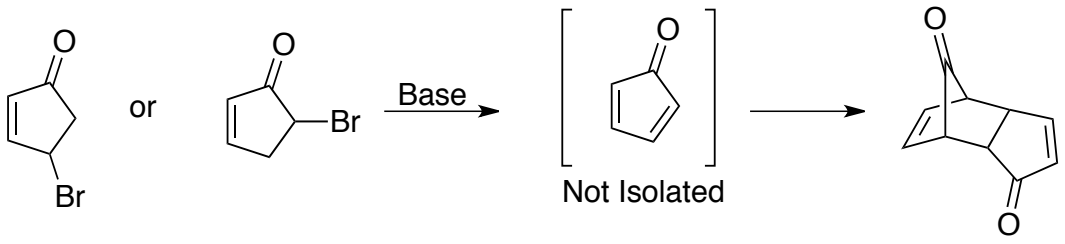


Figure 3.2 In situ generation of cyclopentadienone from 4-Bromo-2-cyclopentenone or 5-Bromo-2-cyclopentenone in the presence of base.

Cyclopentadienone is a valuable synthetic intermediate that is generated in situ from a bromocyclopentenone precursor, **Figure 3.2**.[30,31] Attempts to isolate cyclopentadienone have been pursued but have only lead to the isolation of the dimer due to its high reactivity[30]. Here, we will generate dicyclopentadienone from 4-bromo2-cyclopentenone in the presence of 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU).

3.2 Experimental Results

Preparation of 4-Bromo-2-cyclopentenone.[30] A three neck 250 mL round bottom flask equipped with a magnetic stir bar was charged with 3.06 mL (3.00 g, 36.6 mmol) of 2-cyclopentenone, 6.51 g (36.6 mmol) of N-Bromosuccinimide and 1.50 g (9.1 mmol) of Azobisisobutyronitrile dissolved in 45 mL of carbon tetrachloride. The mixture was refluxed for approximately 2-3 hrs, until ^{1}H NMR showed conversion of starting materials into product. After reaction was completed, it was filtered through a celite plug

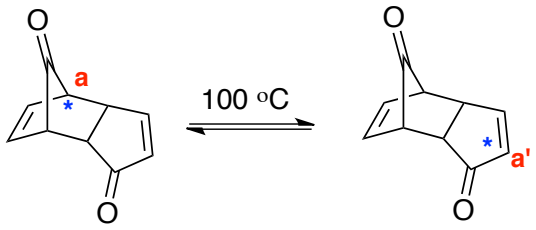
and the cake washed with cold carbon tetrachloride. The filtrate was washed with water and a dilute solution of sodium thiosulfate and then dried over sodium sulfate. The crude product was concentrated under vacuum and purified via column chromatography using silica gel and 20% ethyl acetate in hexanes to afford 3.00 g (51 % Yield) of 4-bromo-2-cyclopentenone as a light yellow oil.

Dimerization of Cyclopentadienone at Low Temperature. A three neck 100 mL round bottom flask equipped with a magnetic stir bar was charged with 2.80 g (17.4 mmol) of 4-bromo-2-cyclopentenone dissolved in 17 mL of dry diethyl ether. The solution was cooled down using a dry ice/acetone bath and the temperature monitored using an internal thermometer. After the temperature was stable to – 78 °C, 2.6 mL (2.65g, 17.4 mmol) of 1,8-diazabicyclo[5.4.0]-7-undecene dissolved in 17 mL of dry diethyl ether were added slowly through an addition funnel to keep the temperature stable within 5 °C. Once addition was completed the reaction was stirred for an additional 30 minutes and then quenched by slowly adding 1.3 mL (1.98 g, 17.4 mmol) of trifluoroacetic acid. Then the reaction mixture was filtered using a büchner funnel and the crude product concentrated under vacuum. Purification of the cyclopentadienone dimer was performed via column chromatography using silica gel and 30% ethyl acetate in hexanes. The reaction afforded 0.4519 g (16 % yield) of the dimer as a white solid.

Dimerization of Cyclopentadienone at Room Temperature. A three neck 100 mL round bottom flask equipped with a magnetic stir bar was charged with 2.50 mL (2.54 g, 16.7

mmol) of 1,8-diazabicyclo[5.4.0]-7-undecene dissolved in 16 mL of dry diethyl ether. The solution was refluxed using an oil bath and the temperature monitored using an internal thermometer. After the temperature was stable to 25 °C, 2.69 g (16.7 mmol) of 4-bromo-2-cyclopentenone dissolved in 16 mL of dry diethyl ether were added slowly through an addition funnel to keep the temperature stable within 5 °C. Once addition was completed the reaction was stirred for an additional 30 minutes and then quenched by slowly adding 1.28 mL (16.7 mmol) of trifluoroacetic acid. Then the reaction mixture was filtered using a buchner funnel and the crude product concentrated under vacuum. Purification of the cyclopentadienone dimer was performed via column chromatography using silica gel and 30% ethyl acetate in hexanes. The reaction afforded 566.6 mg (21 % yield) of the dimer as a white solid.

Equilibration of Dicyclopentadienone. In a typical procedure, 300 mg of pure dicylopentadienone prepared at -78 °C was placed in a pressure tube and heated for 2 h at 100 °C. The resulting dicyclopentadienone was then analyzed by NMR to probe the isotopic distribution at position a versus a'. An alternative equilibration period of only 1 h at 100 °C resulted in an isotopic composition that was indistinguishable by NMR analysis, suggesting that the 2 h equilibration period is sufficient. These results allowed us to decide the highest temperature under which the dimerization of cyclopentadienone can be carried without any equilibration of products, **Figure 3.3**.



Equilibration time	KIE, a/a'
0 hr	0.978(3)
1 hr	0.978(3)
2 hr	0.993(3)

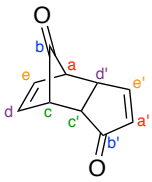
Figure 3.3 Equilibrium isotope effects for the isomerization of dicyclopentadienone at 100 °C.

Experimental Kinetic Isotope Effects. NMR samples were prepared using between 230 mg and 250 mg of cyclopentadienone dimer in 5 mm NMR tubes filled to a constant height of 5 cm with $CDCl_3$. The ^{13}C spectra were recorded at 125.81 MHz using inverse gated decoupling, delays of 22 s for a/a', 156 s for b/b', 26 s for c/c', 24 s for d/d' and 20 s for e/e' between π/2 calibrated pulses and a 7 s acquisition time to collect 406,976 points. Integrations were numerically determined using a constant integration region for each peak that was a constant multiple of the peak widths at half-height. In accordance with the methodology we have previously published, for the integration of each pair of corresponding positions within the cyclopentadienone dimer the transmitter was set half way in between the two peaks of interest on each measurement[5]. A zero-order baseline correction was generally applied, but to avoid any qualitative manipulation no first-order or higher-order baseline correction was ever applied. Six spectra were recorded for each pair of positions on each sample. The assignments of the peaks in the ^{13}C spectrum of

cyclopentadienone dimer was carried by 2D-NMR (HMBC, HSQC and COSY) experiments.

The experimental intramolecular KIEs for the thermal dimerization of cyclopentadienone were measured for two independently prepared samples of dimer at each temperature. The experimental intramolecular KIEs are summarized in **Table 3.1**, and they show a preference to have a greater amount of ^{12}C at the newly formed sigma bonds, similar to what has been previously observed for the dimerization of cyclopentadiene and dimerization of methacrolein.

Table 3.1 Summary of experimental intramolecular KIEs at 195 and 298 K for dimerization of cyclopentadienone. (*only measured for 1 sample)



Position	Temperature = 195 K		Temperature = 298 K	
	Rel. Amount ^{13}C	KIE (x/x')	Rel. Amount ^{13}C	KIE (x/x')
a'/a	1.019(1)	0.981(1)	1.025(3)	0.976(3)
b'/b	1.006(3)	0.994(3)	1.003(4)*	0.997(4)*
c'/c	0.987(2)	1.014(2)	0.993(4)	1.007(4)
d/'d	not determined		not determined	
e'/e	not determined		not determined	

3.3 Computational Results

Choosing the Optimal Method and Basis Set. The method and basis set to be used for the study of the dimerization of cyclopentadienone was done by comparing a high level computational method, G4 on a B3LYP/6-31G* optimized structe, against a series of low cost computational methods and basis sets. The results obtained from these calculations are summarized in **Table 3.2**, they show that M06/6-31+G** energetics are comparable to those obtained from G4.

Table 3.2 Computational methods and basis sets used to explored the energy surface for cyclopentadienone dimerization.

Method	Basis Set	Cope T.S	Monomer	Dimer
G4	/	-8.0	-11.3	-35.8
B3LYP	6-31G*	-6.3	-17.2	-32.1
B3PW91	6-31G*	-9.3	-13.7	-37.1
	6-31G**	-9.1	-13.8	-36.7
	6-31+G*	-9.2	-14.6	-36.3
	6-31+G**	-9.0	-13.8	-36.7
M06	6-31G*	-8.1	-9.5	-37.6
	6-31G**	-7.8	-9.6	-37.1
	6-31+G*	-8.0	-10.3	-36.5
	6-31+G**	-7.8	-10.4	-35.9
M062X	6-31G*	-6.4	-11.2	-39.1

Four stationary points were located along the energy surface using M06/6-31+G** and their structures are shown in **Figure 3.4**. The located saddle points, b and c, show the symmetry of both structures in agreement with Caramella's report[29]. Transition state

structures have only one imaginary frequency while the starting material and product have zero imaginary frequencies.

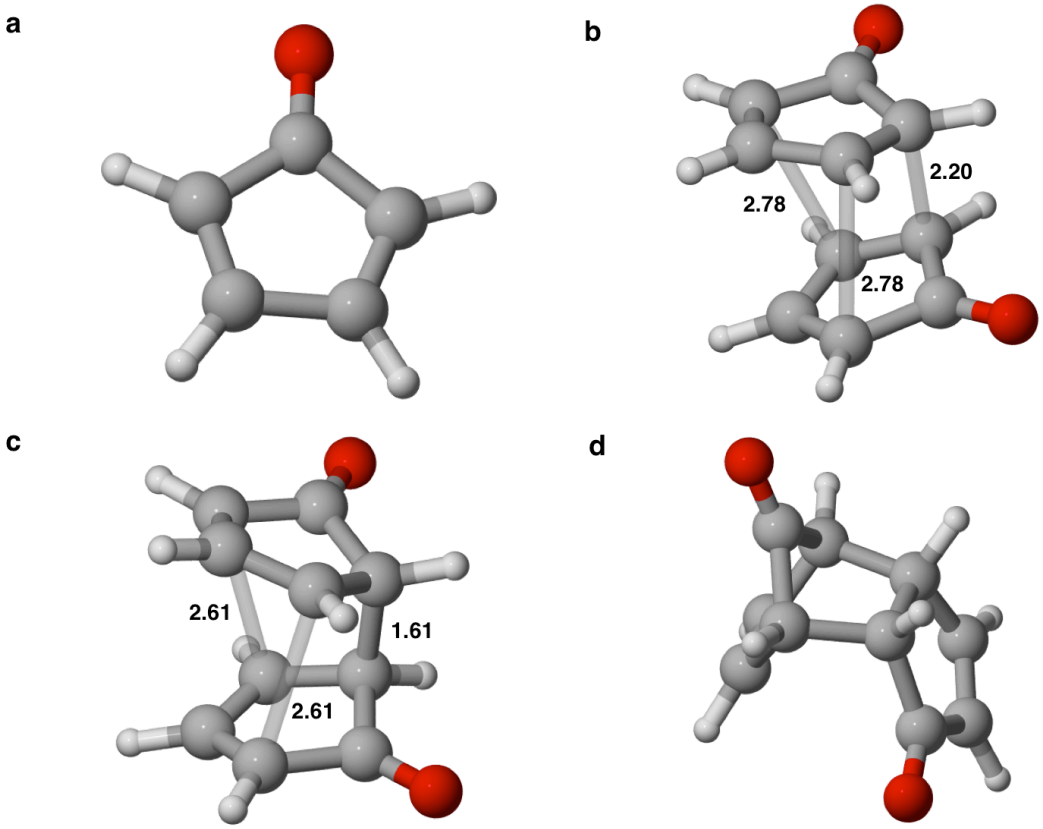


Figure 3.4 Stationary points located on the potential energy surface for cyclopentadienone dimerization in the gas phase using M06/6-31+G**. a. Optimized structure of the starting material. b. Saddle point for the cyclopentadienone dimerization. The structure illustrates the participation of two sets of [4+2] orbital interactions. c. Saddle point corresponding to the Cope re-arrangement for the interconversion between isotopomeric products. d. Optimized structure of the unsymmetrical cyclopentadienone dimer.

Dynamic Trajectories. Direct dynamic trajectories were initialized following an analogous procedure to that employed on Chapter II. In order to over come the computational cost of running dynamic trajectories with a ^{13}C in one of the

cyclopentadienone moieties we took advantage of our trick of starting dynamic trajectories with *in silico*, superheavy carbon atoms. Quasi-classical dynamic trajectories in the gas phase, on a M06/6-31G* energy surface were initialized from isotopomers of the cycloaddition transition state structure, containing a single ^{16}C, ^{20}C, ^{28}C, ^{44}C, ^{76}C, or $^{140}C(12+2^{N}$ amu, **N** =2, 3,4, 5, 6, or 7). Each normal mode in the transition state structure was give its zero point energy (zpe), along with a Boltzman distribution of a sample at 78 or 25 °C, with a random phase. Because the lowest-energy real normal mode in the cycloaddition transition state structure, "mode 3" desymmetrizes the structure in a way that has a large effect on trajectory outcomes, an equal number of trajectories were given positive versus negative velocities in this mode. The transition vector was given a Boltzmann sampling of energy 'forward' from the col. The trajectories were integrated until either the product was formed (median time 80 fs) or the starting materials were reformed and the results are summarized in **Table 3.3** and **Table 3.4**.

Table 3.3 Quasi-classical dynamic trajectories initialized from the cycloaddition transition state structure on a M06/6-31G* energy surface at 298 K.

Position / mass	Total Runs	Total x	Total x'	Recrossed	KIE, x/x'
a/a' 140	9016	3787	5229	252	0.72 ± 0.03
a/a' 76	6554	2801	3753	182	0.75 ± 0.04
a/a' 44	6493	2881	3612	193	0.80 ± 0.03
a/a' 28	8240	3819	4421	248	0.86 ± 0.03
a/a' 20	11215	5323	5892	289	0.90 ± 0.03
a/a' 16	19730	9654	10076	548	0.96 ± 0.03
			extrapolated to ^{13}C 0.984		
b/b' 140	7459	3633	3826	151	0.95 ± 0.04
b/b' 76	7302	3625	3677	188	0.99 ± 0.04
b/b' 44	10137	5085	5052	257	1.01 ± 0.04
c/c' 140	8536	6070	2466	224	2.46 ± 0.05
c/c' 76	5161	3427	1734	115	1.98 ± 0.05
c/c' 44	5505	3381	2124	131	1.59 ± 0.03

Dynamic trajectories correctly predict the major product in each case, and the magnitude of the selectivity in the trajectories follows the same trend as in the experimental KIEs. As the mass of the "super heavy" carbon atoms is increased the selectivity of the reaction is also increased in all positions. Trajectories with a label on position b exhibit a small selectivity with a heavy carbon of mass 140 amu, but with ^{76}C very small selectivity was observed. A minimal amount of recrossing is observed, however the Newtonian preference to place the lighter atoms at the newly formed sigma bond predominates.

Table 3.4 Quasi-classical dynamic trajectories initialized from the cycloaddition transition state structure on a M06/6-31G* energy surface at 195 K.

Position / mass	Total Runs	Total x	Total x'	Recrossed	KIE, x/x'
a/a' 140	9278	3838	5440	294	0.71 ± 0.03
a/a' 76	6559	2794	3765	211	0.74 ± 0.04
a/a' 44	7433	3367	4066	219	0.83 ± 0.03
a/a' 28	8238	3853	4385	234	0.88 ± 0.03
a/a' 20	13085	6289	6796	355	0.93± 0.03
a/a' 16	21644	10562	11082	642	0.95 ± 0.02
			extrapolated to ^{13}C 0.985		
b/b' 140	11556	5655	5901	328	0.96 ± 0.03
b/b' 76	6924	3423	3501	195	0.98 ± 0.04
c/c' 140	8628	6511	2117	242	3.08 ± 0.07
c/c' 76	6419	4449	1970	173	2.26 ± 0.05
c/c' 44	7074	4519	2555	202	1.77 ± 0.03

In order to evaluate whether dynamic trajectories accurately predict the experimental observations of a temperature independent KIEs, we initialized a second set of quasicalssical dynamic trajectories at 195 K. The computationally calculated KIEs at 195 K (**Table 3.3**) are statistically indistinguishable from those at 298 K (**Table 3.4**). Dynamic trajectories at both temperatures are in good agreement with experimental intramolecular KIEs for the dimerization of dicyclopentadienone.

The uncertainties in the trajectory ratios were calculated by setting up an Excel spreadsheet that would repeatedly simulate the complete set of trajectory runs with each choice of superheavy carbon. In the simulations, the outcome of each individual trajectory depended on a random number and on a weighting that corresponded to the ratio of outcomes actually observed in the set of trajectories. Because of the weighting,

the average outcome of an infinite number of Excel simulations would be equal to the outcome observed in the trajectories. Each individual simulation, however, departs from the observed outcome in a way that reflects the role of random chance on the results in a set of trajectories. From the results of 119 simulations, standard deviations was calculated: mass-140: 0.018; mass 76 0.022; mass 44 0.025; mass 28 0.018. The 95% confidence ranges would be twice these standard deviations.

Extrapolation of Trajectory Results to ^{13}C. The process for extrapolation of the trajectory results to ^{13}C starts with the assumption that the additional isotope effect per additional mass unit decreases as the mass grows. For example, the effect of going from ^{13}C to ^{14}C would be larger than the effect of going from ^{140}C to ^{141}C. We further assumed that this decrease with mass is nonlinear with a decreasing slope, that is, that a plot **(Figure 3.5)** of the additional isotope effect per additional mass versus mass would have a greater slope at low masses (e.g., ^{13}C to ^{14}C) than at high masses (e.g. ^{140}C to ^{141}C). These simple assumptions exclude some extrapolation processes that would lead to physically unreasonable isotope effects at both high masses and at ^{13}C.

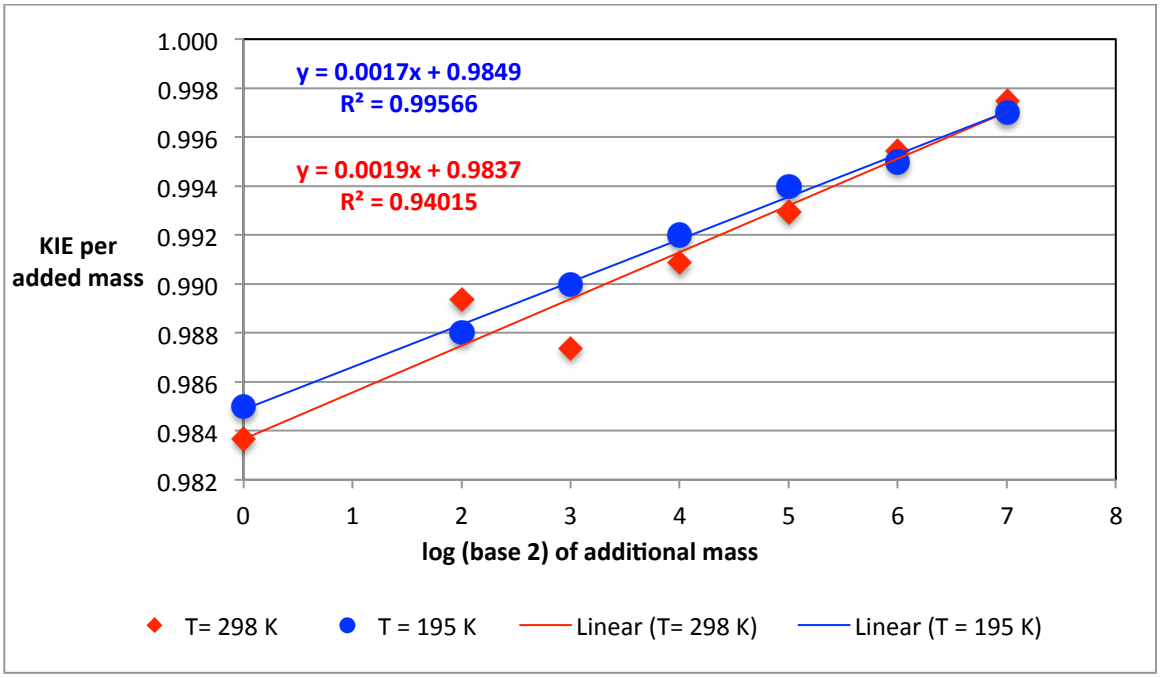


Figure 3.5 ^{13}C extrapolated KIE for a/a' at 195 K and 298 K from quasiclassical dynamic trajectories on Table 3.3 and Table 3.4. The corresponding equation that describes the trendline at each temperature are also shown.

Tables 3.3 and 3.4 and the associated graph show the data used in the extrapolation, the extrapolated results, and the complete linear regression analysis and statistics. The Nominal KIEs come from the **Table 2.2** on the previous section. The "additional mass" is defined as the mass beyond 12 amu. The "isotope effect per mass" is defined as the geometric average. The extrapolation was then carried out by assuming a linear relationship between the log of the additional mass (the base is arbitrary but set conveniently here as 2) versus the isotope effect per mass. The extrapolation process used the Regression tool in Microsoft Excel 2011 for Mac,Version 14.3.9

3.4 Discussion

The dimerization of cyclopentadienone constitutes a third example of Newtonian KIEs. These KIEs are characterized for the preference of placing lighter isotopes at the newly formed sigma bonds in Diels-Alder reactions as a result of the classical effect of mass difference between isotopes without the contribution of ZPE. The relatively fast Diels-Alder reaction of cyclopentadienone with itself and thermal stability of the monomer and dimer makes this reaction ideal to study the temperature dependence of Newtonian isotope effects. A combined experimental and computational approach was taken in order to validate our hypothesis of temperature independent KIEs. Experimental intramolecular KIEs at 195 K and 298 K remain unchanged for position a. Quasiclassical dynamic trajectories are in good agreement with experimental results by predingting the ^{13}C KIEs for por position a at 195 K as 0.985 versus an experimental KIE 0.980(2) at the same temperature. The extrapolated ^{13}C KIE from dynamic trajectories at 298 K was 0.984 versus an experimental KIE 0.976(3). This suggest that these isotope effects, at least for positions a versus a' and b versus b', are relatively insensitive to temperature within a range of 100 degrees, as was shown on the plotted dynamic trajectories for position a at both temperatures.

The predicted experimental and computational KIE for position c versus c' also follows a Newtonian behavior, however the KIE changes as the temperature changes. This isotope effects shows a kinetic behavior as the temperature changes. Due to limitations related to NMR separation of the lines for positions d and e, KIEs for d/d' and e/e' could

not be calculated. Lines for the olefinic carbons where too close to each other making it difficult to phase and cut spectra collected for such purpose.

CHAPTER IV

TUNNELING IN THE RING-OPENING/OXIDATION OF CYCLOPENTOXY RADICAL

4.1 Introduction

Tunneling is a quantum mechanical phenomenon by which a molecular structure passes through a barrier, a forbidden region, rather than over a barrier. Deviations from normal kinetics that lead to dramatic increase in the rate of reactions, large KIEs and curvatures in Arrhenius plots that lead to abnormal activation energies and A factor have been utilized as a diagnostic for tunneling. Three General trends can impact quantum tunneling in chemical reactions. First, lighter masses are known to tunnel more easily than heavier masses. As a result, hydrogen tunnels more than deuterium and the observation of large H/D KIEs has been a common diagnostic for tunneling.[32-35] Due to the mass effect, tunneling was long thought to be non-existent or negligible for heavy-atoms. Tunneling is known to significantly enhance the rate of reactions that have high barriers. A second trend is that tunneling occurs more rapidly though narrow barriers.[36,37] A well studied case is the isomerization of cyclobutadiene. Carpenter reported that below 0 °C tunneling is responsible for 97% of isomerization.[37] Third, tunneling contribution is greater at lower temperatures since molecules do not have the required energy to overcome high barriers. At times this results in the observation of reactions that simply would not occur at all without tunneling, and the best-established tunneling effects have been observed at cryogenic temperatures.[38-46]

However, these trends are not absolute requirements for tunneling. Recently, a large number of examples where heavy-atom tunneling has been experimentally identified in chemical reactions have been reported.[37-39,43,45,46] Furthermore, the combination of experimental and computational results has greatly ease the process of identifying tunneling in chemical reactions. In 2012, our group reported a study about the tunneling contribution in the Roush allylboration of aldehydes by employing a combination of experimental KIEs and theoretically predicted isotope effects.[45]

The cleavage of alkyl groups from alkoxy radicals is a reaction of importance in combustion chemistry[47,48], atmospheric chemistry[49-53], polymer chemistry[54], biological chemistry[55-57], and synthetic organic chemistry[58-63]. The branching ratio of among cleavage processes has been of significant interest in all of these areas, and much work has been directed at the understanding and accurate prediction of the ratio of cleavage products, **Figure 4.1**. We have become interested in the degree to which the selectivity in this fundamental reaction is affected by tunneling and other dynamic effects not accounted for in conventional transition state theory.

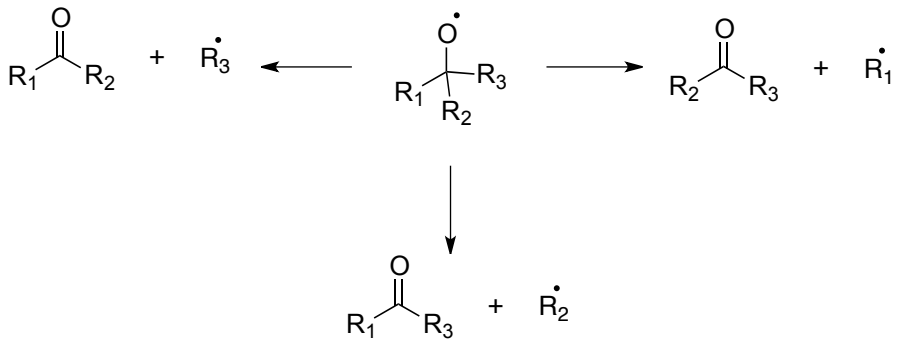


Figure 4.1 Branching in the cleavage of alkyl radicals from an alkoxy radical.

A simple reaction involving alkoxy radicals is the free-radical chain decomposition of tertiary alkyl hypochclorites, **Figure 4.2**.[58,64]

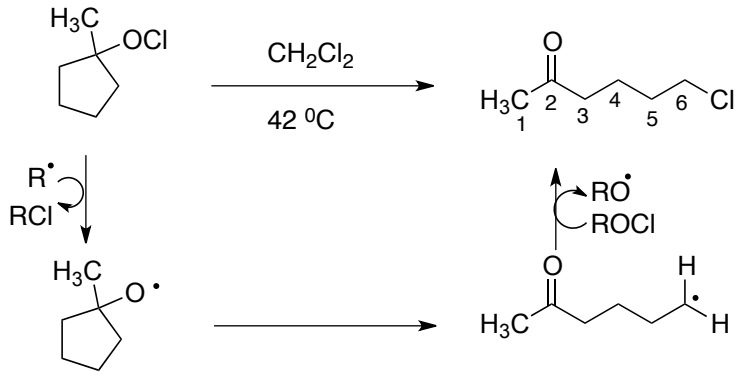


Figure 4.2 Transformation of 1-Methylcyclopentoxy hypochlorite to 6-Chloro-2-hexanone via a radical mechanism.

We choose to study the ring-opening decomposition of 1-methylcyclopentyl hypochlorite because of its facile and quantitative ring opening to afford 6-chloro-2-hexanone and because the ^{13}C isotopic distribution in the product is readily analyzed and provides a convenient handle on tunneling in the reaction, **Figure 4.3**.

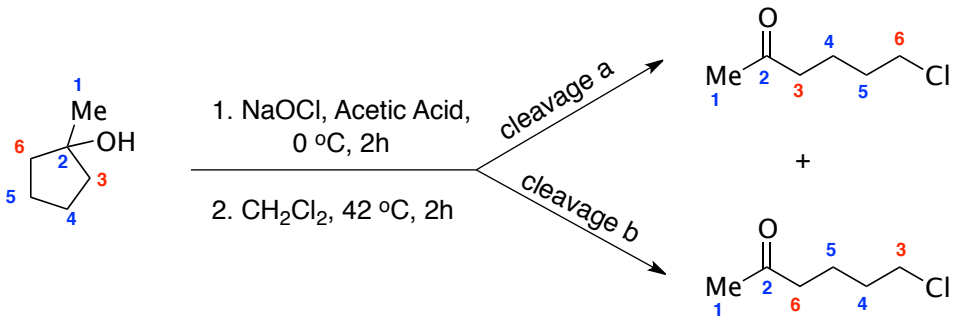


Figure 4.3 Ring-opening/oxidation reaction of 1-Methylcyclopentanol.

Because of the symmetry of the generated alkoxy radical, to posibble cleavage sites are available, a or b, and the ration of the amount of cleavage a versus cleavage b constitutes an intramolecular KIE. By measuring the relative content of ^{13}C at C-3 versus C-6 on the product using our NMR methodology will provide the intramolecular KIE. In order to study the tunneling contribution in this reaction experimental KIEs will be compared against theoretically predicted isotope effects.

4.2 Experimental Results

Preparation of 6-Chloro-2-hexanone.[65] A sample of 3.00 grams (29.9 mmol) of 1-methylcyclopentanol was added into a round bottom flask equipped with a magnetic stir bar along with a 44.6 ml (2.2 g, 29.9 mmol) of a 5% sodium hypochlorite solution. The solution was cooled down to 0 °C and 1.71 mL (29.9 mmol) of acetic acid were added slowly. The mixture was stirred at 0 °C for 2 hours and then washed with 20 mL of a saturated solution of sodium bicarbonate and extracted using 30 mL of dichloromethane. The organic extract was refluxed for 2 hours at 42 °C. The crude product was washed

with a saturated solution of sodium bicarbonate and extracted using of dichloromethane to remove any unreacted alcohol. The product was then concentrated under vacuum.

Experimental Kinetic Isotope Effects. NMR samples were prepared using 300 mg of 6-chloro-2-hexanone in 5 mm NMR tubes filled to a constant height of 5 cm with $CDCl_3$. The ^{13}C spectra were recorded at 125.81 MHz using inverse gated decoupling, delays of 26 s between $\pi/2$ calibrated pulses and a 7 s acquisition time to collect 603,448 points. Integrations were numerically determined using a constant integration region for each peak that was a constant multiple of the peak widths at half-height. In accordance with the methodology we have previously published, for the integration of each pair of corresponding positions within the methacrolein dimer the transmitter was set half way in between the two peaks of interest on each measurement.[5] A zero-order baseline correction was generally applied, but to avoid any qualitative manipulation no first-order or higher-order baseline correction was ever applied. Six spectra were recorded for each sample. The assignments of the peaks in the ^{13}C spectrum of 6-chloro-2-hexanone were done using HMBC, HSQC and COSY 2-D NMR techniques.

The experimental intramolecular KIEs for the ring opening of 1-methylcyclopentoxy radical were measured for two independently prepared samples of 6-chloro-2-hexanone at 42 °C. The experimental intramolecular KIE is summarized in **Figure 4.4**.

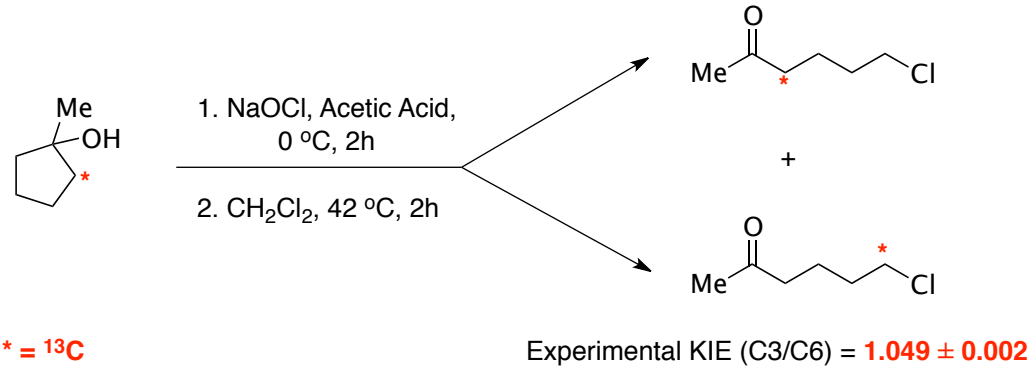


Figure 4.4 Experimental intramolecular KIEs at natural abundance for the ring-opening of 1-Methylcyclopentanol.

The KIE reflects a greater content of ^{12}C on C-6 and more ^{13}C on position C-3 of the product. A large normal intramolecular isotope effect exhibits the preference of cleaving the C-C bond that has greater content of ^{12}C over ^{13}C. In order to further investigate whether the origin of this isotope effect is affected by tunneling or any other form of dynamic effects we employed computational tools that could aid in such cases. The computational approach that was taken in order to investigate our hypothesis is presented on the section below.

4.3 Computational Results

Choosing the Optimal Method and Basis Set. Computational studies were employed to aid in the interpretation of the experimental isotope effects. B3LYP was chosen as the ideal method for our studies since it has been shown that it accurately predicts the energetics and thermodynamic and kinetic properties of radicals.[66,67] A fully optimized transition state structure, starting material, and product were obtained using UB3LYP/6-31G* in the gas phase.

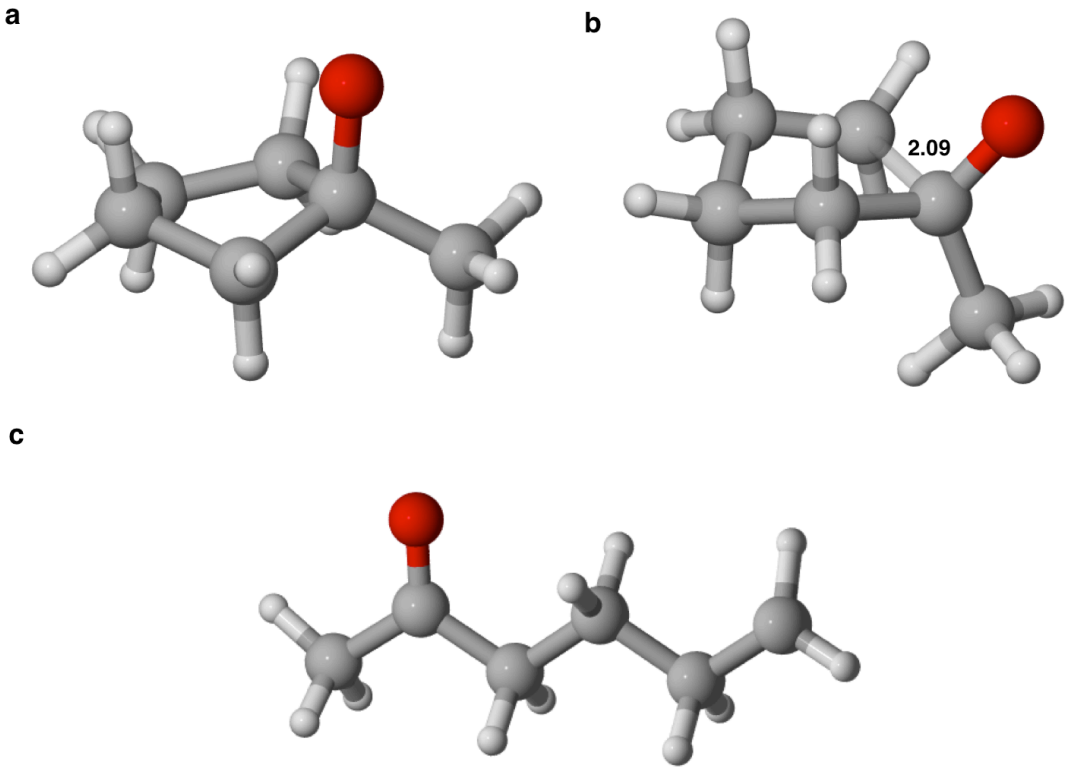


Figure 4.5 Stationary points located on the energy surface for the ring-opening of 1-Methylcyclopentoxy radical using UB3LYP/6-31G* in the gas phase. a. Optimized structure for the 1-methylcyclopentoxy radical. b. Transition state structure for the cleavage of the alkoxy radical. c. Optimized product structure of the alkyl radical generated upon the cleavage of the alkoxy radical.

The calculated UB3LYP/6-31G* potential energy barrier for this reaction was estimated to be 9.7 kcal/mol. The estimated barrier is in good agreement with a high level computational method, UCCSD(T)/cc-pvdz (9.4 kcal/mol), and within experimental observations. The transition state structure b has exactly one imaginary frequency, shown on **Figure 4.5**, and was utilized in the computational prediction of intramolecular KIEs.

Prediction of Kinetic Isotope Effects. In order to study the role that Quantum tunneling plays in the experimental KIEs shown on Table 4.1, the KIEs were computed both with and without inclusion of tunneling. Since TST predictions do not account for tunneling and recrossing contribution, predictions were also carried for Canonical Variational Transition State Theory[10] (CVT) with the effect of multidimenstional tunneling contribution using the Small Curvature Tunneling[68] (SCT) approximation. The prediction of small KIEs by the CVT/SCT method has the problem that tight convergence criteria and small step sizes are required for sufficient numerical convergence. However, due to the small size of the system under study the computational time was very short. These calculations were performed using GAUSSRATE[69] as the interface between POLYRATE[12] and Gaussian 09[70]. The semiclassical rate constants were computed using the Page-McIver method[71] to follow the minimum energy path (MEP) with a step size of 0.005 bohr. The predicted TST and CVT/SCT KIEs for C-3 versus C-6 were computed from the rate constants obtained from the parent calculation (all carbon atoms being ^{12}C) and calculations with a ^{13}C label at the carbon atom being broken at the transition state. Computationally predicted KIEs showed a small contribution from heavy-atom tunneling on the selectivity of this reaction, **Table 4.1**. Although tunneling contribution for this reaction is small at 42 °C, TST or CVT cannot account for the experimentally observed KIE. On the other hand, CVT/SCT accurately predicts the experimental KIE observer for this reaction.

Table 4.1 Summary of experimental and UB3LYP/6-31G* predicted KIE.

Relative Content of ^{13}C		**Experimental KIE**	
C-3	C-6	C6/C3	
1000	953.270	1.049 ± 0.002	
B3LYP/6-31G* Predicted KIEs			
TST	CVT	TST/SCT	CVT/SCT
1.044	1.041	1.051	1.050

The agreement between experimental KIE and computationally predicted KIE from CVT/SCT supports the role of tunneling as a contributor in the selectivity if the cleavage of 1-methylcyclopentoxy radical.

A theoretical Arrhenius plot for CVT and CVT/SCT within a temperature range of 100 – 400 Kelvin was also generated from POLYRATE calculations, **Figure 4.6.** The CVT/SCT Arrhenius plot shows a small curvature that is characteristic for reactions where tunneling has been identified.

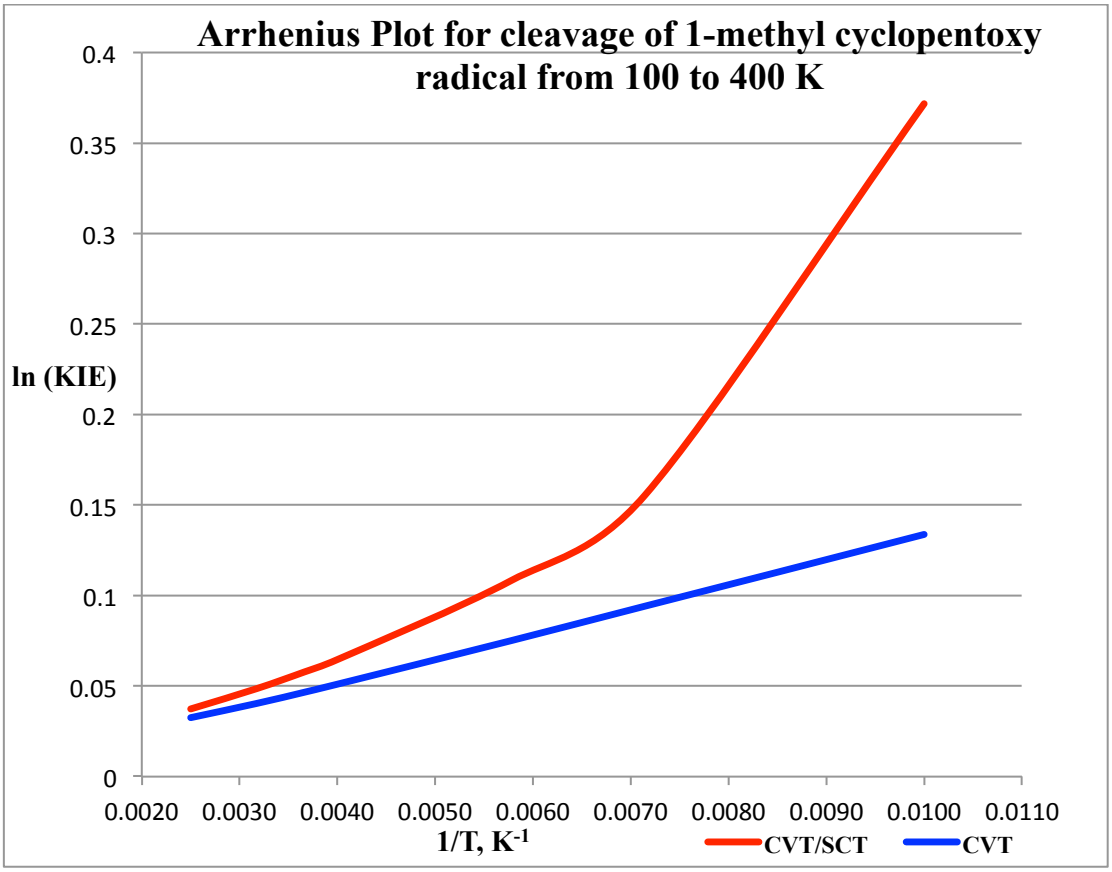


Figure 4.6 Arrhenius plot of the CVT and CVT + SCT ^{13}C KIEs for the ring-opening of cyclopentoxy radical from 100 to 400 K.

4.4 Discussion

The general trends that impact tunneling have long suggested that this quantum phenomenon is most likely to be observed for lighter masses, in reactions with relatively high barriers, broad barrier widths and or at lower temperatures. Here we have reported an example where tunneling has been shown to contribute in a reaction with an ordinary barrier width at an elevated temperature. The contribution of quantum tunneling in the cleavage of 1-methylcyclopentoxy radical is not accounted for by TST and for this reason the predicted KIE for this reaction is underestimated. Although tunneling

contribution is small, less than 1%, for this reaction it does impact the experimental KIE for this reaction. The consideration of tunneling correction is necessary in order to accurately predict the experimental KIE. The predicted KIE from CVT/SCT is in excellent agreement with experimental observations. In addition, it has been shown that the use of computational chemistry helps in the process of elucidating tunneling contribution of chemical reactions. Although experimental KIE was only measured at 42 °C the theoretical Arrhenius plot allows to observed how tunneling contribution increased at lower temperatures and statistical rate theories predictions of the KIE deviate significantly when no tunneling correction is taken into consideration. In conclusion, tunneling is present in all reactions regardless of barriers heights, temperature, or barrier widths. The real issue about tunneling is whether this phenomenon impacts the kinetics of a particular reaction and whether we can experimentally detect its contribution in chemical reactions.

CHAPTER V

NON-STATISTICAL BEHAVIOR IN THE CLEAVAGE OF ALKOXY RADICALS

5.1 Introduction

The the branching ratio that results from the cleavage of alkyl groups on tertiary alkoxy radicals is of great interest in combustion chemistry, atmospheric chemistry, polymer chemistry, biological chemistry, and synthetic organic chemistry as stated on chapter IV. Chapter IV illustrates the contribution of tunneling on the ring-opening of 1-methylcyclopentoxy radical and we are interested on the contribution of dynamic effects, not accounted for conventional transition state theory, in the selectivity of this fundamental reaction in other systems.

Experimental observations by Dowd and Colleagues[60], showed that upon formation of tertiary alkoxy radicals on bicyclo[2.2.2]- and bicyclo[4.2.0]octenones cleave to afford the thermodynamically less-stable product, **Figure 5.1**.

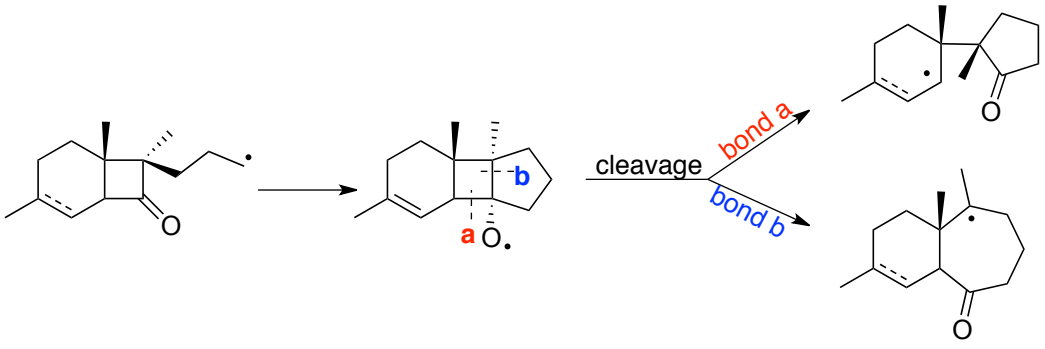
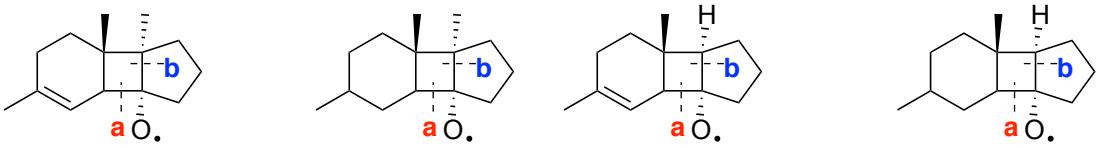


Figure 5.1 Cleavage of a tertiary tricyclic alkoxy radical.[60]

In contrast to the expected preference for the formation of an allylic radical from cleavage of bond a, the radical formed from cleavage of bond b is observed as the major experimental product. This surprising observation led Dowd to investigate the role of radical stability by conducting experiments on a substrate without an olefin that would stabilize the radical, **Figure 5.2**. However, the presence of an olefin to stabilize the radical formed from bond a cleavage does not change significantly the experimental product ratio of cleavage a versus cleavage b.



cleavage a: 11 % cleavage b: 80 %	cleavage a: 22 % cleavage b: 68 %	cleavage a: Not observed cleavage b: 62 %	cleavage a: 14 % cleavage b: 49 %

Figure 5.2 Structural and substituent effects studied by Dowd in the cleavage of tricyclic alkoxy radicals.[60]

This led Dowd to postulate the possibility of a deactivating effect of the olefin on the cleavage of bond a. Upon removal of the angular methyl group in the substrate under study no product from cleavage a was detected experimentally, suggesting that the methyl group has little or no impact on cleavage of bond a.

Few years later, Houk[72] reported a computational study in order to elucidate the origin of the unexpected cleavage of these tertiary alkoxy radicals. This study utilized a combination of CASSCF, UHF, and B3LYP functionals with 6-31G* as the basis set.

Computational invesitigations showed that the transition state structures for the cleavage of a series of alkoxy radicals are early, and therefore stabilization of the radical by the adjacent olefin does not take place at the transition state region. Calculations also showed that the rate for cleavage of bond a is slower than the rate for bond b cleavage, in agreement with experimental observations. Regarding substitution effects on the branching ratio for alkoxy radical cleavages, it was concluded that methyl group substitution at the alkoxy carbon has very small amount of transition state stabilization, while substitution at the radical forming carbon has a larger stabilization effect at the transition state. Although the reported computational predictions are in good agreement with experimental observations, the methods employed on this study (CASSCF and UHF) tend to overestimate the activation energies of reactions that involve radical species. On the other hand, B3LYP ability treating radical species still questionable as at may underestimate the barrier for these reactions. An indicator of this, is the note made by the author stating that transition state structures for cleavage of bond a on B3LYP had converge issues. The use of inappropriate methods on Houk's computational study raises the possibility of inaccuracy on the energetics of these reactions. This could result in that some of the located transition state structures may not be real and statistical rate models may not be useful on explaining the origin of the regioselectivity on alkoxy radical cleavage.

Another important issue that is often ignored is that alkoxy radicals are generated with excess energy as a result from the cleavage of an O-O or O-X bond, **Figure 5.3**. Since

alkoxy radicals are short-lived species they react as "hot-intermediates" before the excess energy can be equilibrated within the molecule. For these reasons we envision that dynamic effects could play an important role in the selectivity of alkoxy radicals cleavage. In addition,

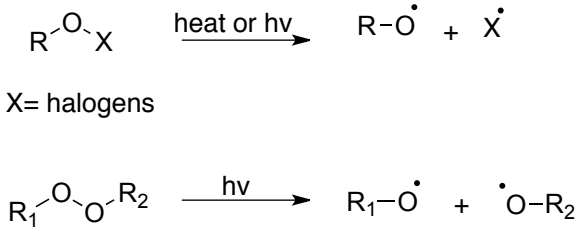


Figure 5.3 Generation of alkoxy radicals from hypohalites and peroxides.

This chapter will study the cleavage of a series of tertiary cyclic alkoxy radicals using a combination of experimental intramolecular KIEs and computational prediction of KIEs to explore the accuracy of statistical theories versus structure.

5.2 Experimental Results

Preparation of 1-Methylcyclobutanol. To 21.4 mL of a 3M solution of methylmagnesium bromide (64.2 mmol) in ether was added dropwise 3.00 g (3.21 mL, 42.8 mmol) of cyclobutanone. After addition of the ketone was completed, the reaction was stirred for an additional 30 minutes and then quenched with a solution of sodium hydrogen sulfate. The product was extracted with ether and dried over sodium sulfate. ^{1}H and ^{13}C NMR showed quantitative conversion of starting materials into products. The reaction yielded 904.9 mgram (10.5 mmol, 25% yield) of product obtained as a clear oil.

Preparation of 5-Chloro-2-pentanone.[65] A sample of 900 mgram (10.5 mmol) of 1-methylcyclobutanol was added into a round bottom flask equipped with a magnetic stir bar along with a 15.6 ml (0.78 g, 10.5 mmol) of a 5% sodium hypochlorite solution. The solution was cooled down to 0 °C and 0.60 mL (10.5 mmol) of acetic acid were added slowly. The mixture was stirred at 0 °C for 2 hours and then washed with 15 mL of a saturated solution of sodium bicarbonate and extracted using 30 mL of dichloromethane. The organic extract was refluxed for 2 hours at 42 °C. The crude product was washed with a saturated solution of sodium bicarbonate and extracted using dichloromethane to remove any unreacted alcohol. The product was then concentrated under vacuum and recovered 841.1 mgram (7.0 mmol, 67% yield) as a light yellow oil.

Experimental KIEs for 5-Chloro-2-pentanone. NMR samples were prepared using 315 mg of 5-chloro-2-pentanone in 5 mm NMR tubes filled to a constant height of 5 cm with $CDCl_3$. The ^{13}C spectra were recorded at 125.81 MHz using inverse gated decoupling, delays of 31 s between $\pi/2$ calibrated pulses and a 7 s acquisition time to collect 603,448 points. Integrations were numerically determined using a constant integration region for each peak that was a constant multiple of the peak widths at half-height. In accordance with the methodology we have previously published, for the integration of each pair of corresponding positions within the methacrolein dimer the transmitter was set half way in between the two peaks of interest on each measurement.[5] A zero-order baseline correction was generally applied, but to avoid any qualitative manipulation no first-order or higher-order baseline correction was ever applied. Eight spectra were recorded for

each sample. The assignments of the peaks in the ^{13}C spectrum of 5-chloro-2-pentanone were done using HMBC, HSQC and COSY 2-D NMR techniques.

The experimental intramolecular KIE at natural abundance for 5-chloro-2-pentanone is presented on **Figure 5.4**.

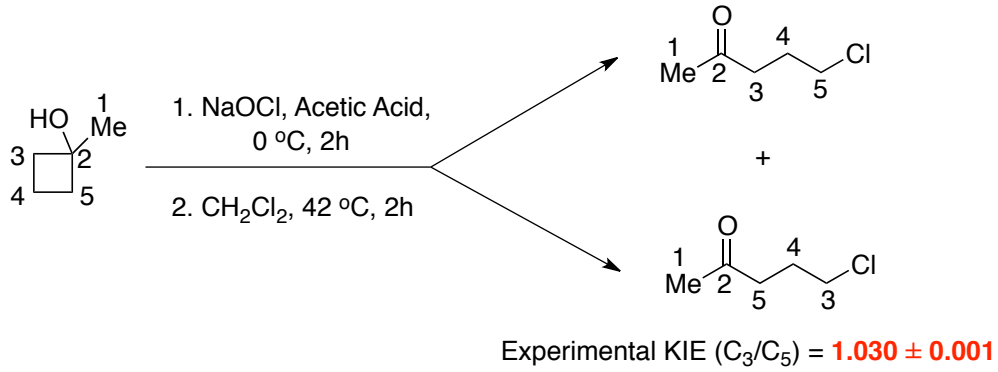


Figure 5.4 Summary of experimental intramolecular KIEs at natural abundance for two independently prepared samples of 5-Chloro-2-pentanone and its associated 95% confidence interval.

The ration of the relative content of ^{13}C at C_3 versus C_5 at the product from the cleavage of 1-methylcyclobutoxy radical constitutes an intramolecular KIE. The normal KIE reflects the preference for the cleavage of the C-C bond adjacent to the alkoxy radical with greater content of ^{12}C.

Preparation of 1-Phenylcyclopropanol.[73,74] To a solution of 2.72 grams (20 mmol) of methylbenzoate and 8.00 grams (8.33 mL, 28 mmol) of Titanium(IV) isopropoxide in 28.0 mL of dry THF was added dropwise 28.0 mL (56 mmol) of a 3M solution of ethylmagnesium chloride in THF. The reaction was stirred overnight at room

temperature, and then quenched by adding distilled water. Salts were removed by filtration and the filtrate washed with ether (3X60mL). The organic layer was washed with water and dried over magnesium sulfate and concentrated under vacuum. Purification of the crude was performed via column chromatography using silica gel and 10% ethylacetate in hexanes. The product was isolated in a mixture (1.57 g, 11.7 mmol, 59% yield) of 1-phenylcyclopropanol and 1-phenylpropanol in 3.3:1 ratio as a yellow oil.

Preparation of 3-Chloropropiophenone.[65] A sample of 3.20 grams (77% purity, 2.4 g, 17.9 mmol) of 1-methylcyclobutanol was added into a round bottom flask equipped with a magnetic stir bar along with 26.6 ml (1.33 g, 17.9 mmol) of a 5% sodium hypochlorite solution. The solution was cooled down to 0 °C and 1.03 mL (17.9 mmol) of acetic acid were added slowly. The mixture was stirred at 0 °C for 2 hours and then washed with 15 mL of a saturated solution of sodium bicarbonate and extracted using 30 mL of dichloromethane. The product was then dried over sodium sulfate and concentrated under vacuum. Purification of the crude was performed via column chromatography using silica gel and 10% ethylacetate in hexanes. The product was isolated as a white solid and the reaction yielded 537 mgram (3.2 mmol, 18% yield) of 3-chloro-1-phenylpropanone.

Experimental KIEs for 3-Chloropropiophenone. NMR samples were prepared using 320 mg of 3-chloro-1-phenylpropanone in 5 mm NMR tubes filled to a constant height

of 5 cm with $CDCl_3$. The ^{13}C spectra were recorded at 125.81 MHz using inverse gated decoupling, delays of 15 s between $\pi/2$ calibrated pulses and a 7 s acquisition time to collect 583,332 points. Integrations were numerically determined using a constant integration region for each peak that was a constant multiple of the peak widths at half-height. In accordance with the methodology we have previously published, for the integration of each pair of corresponding positions within the methacrolein dimer the transmitter was set half way in between the two peaks of interest on each measurement.[5] A zero-order baseline correction was generally applied, but to avoid any qualitative manipulation no first-order or higher-order baseline correction was ever applied. Six spectra were recorded for each sample. The assignments of the peaks in the ^{13}C spectrum of 3-chloro-1-phenylpropanone were done using HMBC, HSQC and COSY 2-D NMR techniques.

The experimental intramolecular KIEs for the ring opening of 1-phenylcyclopropoxy radical were measured for two independently prepared samples of 3-chloropropiophenone at 0 °C. The experimental intramolecular KIE is summarized in **Figure 5.5**.

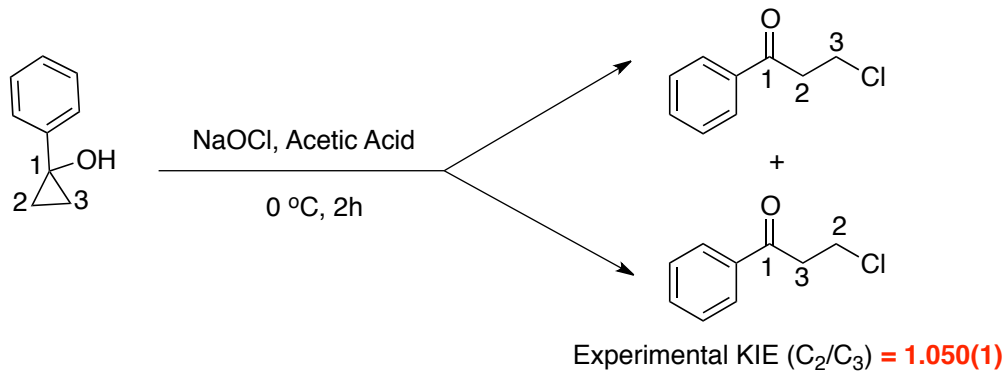


Figure 5.5 Summary of experimental intramolecular ^{13}C KIEs at natural abundance for two independently prepared samples of 3-Chloropropiophenone and the associated 95% confidence interval.

The KIE reflects a greater content of ^{12}C on C-3 and more ^{13}C on position C-2 of the product. A large normal intramolecular isotope effect exhibits the preference of cleaving the C-C bond that has greater content of ^{12}C over ^{13}C. In order to further investigate whether the origin of the experimenatl isotope effects presented on this chapter are affected by tunneling or any other form of dynamic effects we employed computational tools that could aid in such cases. The computational approach that was taken in order to investigate our hypothesis is presented on the section below.

5.3 Computational Results

Choosing the Optimal Method and Basis Set. Computational studies were employed to aid in the interpretation of the experimental isotope effects. M11 was chosen as the ideal method for our studies since it has a minimal root mean square error with the smallest practical basis set against CCSDTT/cc-pvDZ and CCSDT/cc-pvTZ calculations. A fully

optimized transition state structure, starting material, and product were obtained using UM11/6-31+G** in the gas phase, **Figure 5.6** and **Figure 5.7**.

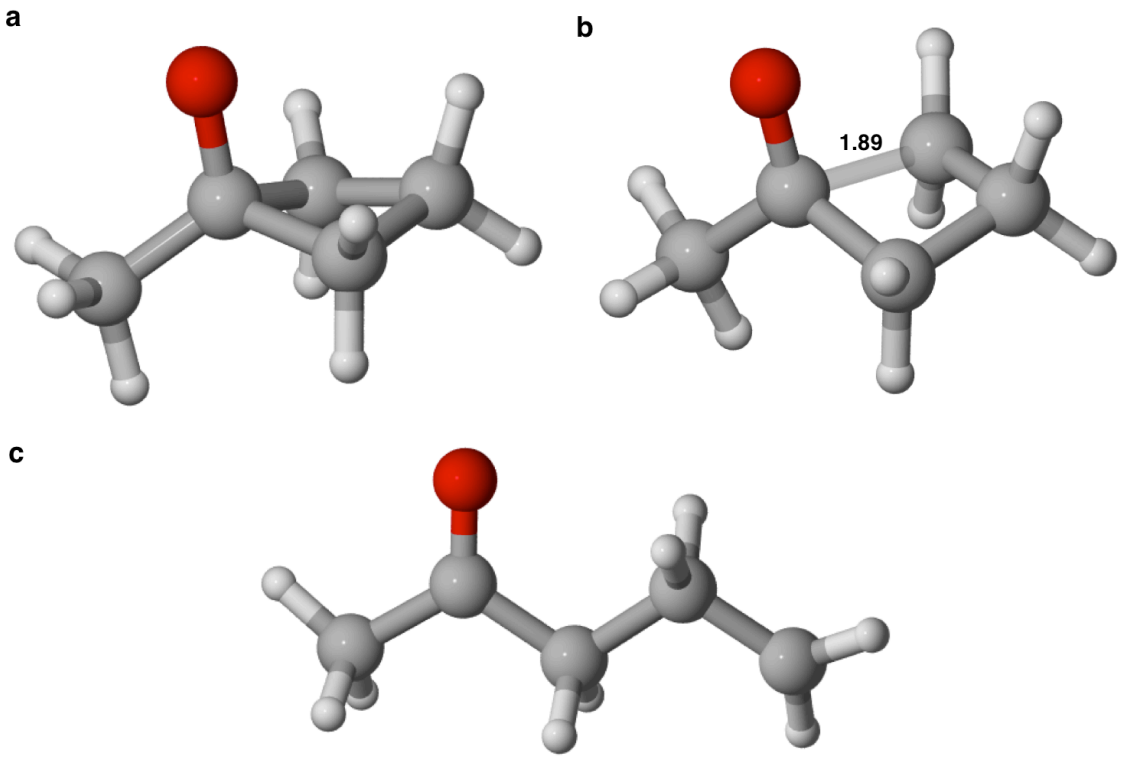


Figure 5.6 Stationary points located on the energy surface for the ring-opening of 1-Methylcyclobutoxy radical using UM11/6-31+G** in the gas phase. a. Optimized structure for the 1-methylcyclobutoxy radical. b. Transition state structure for the cleavage of the alkoxy radical. c. Optimized product structure of the alkyl radical generated upon the cleavage of the alkoxy radical.

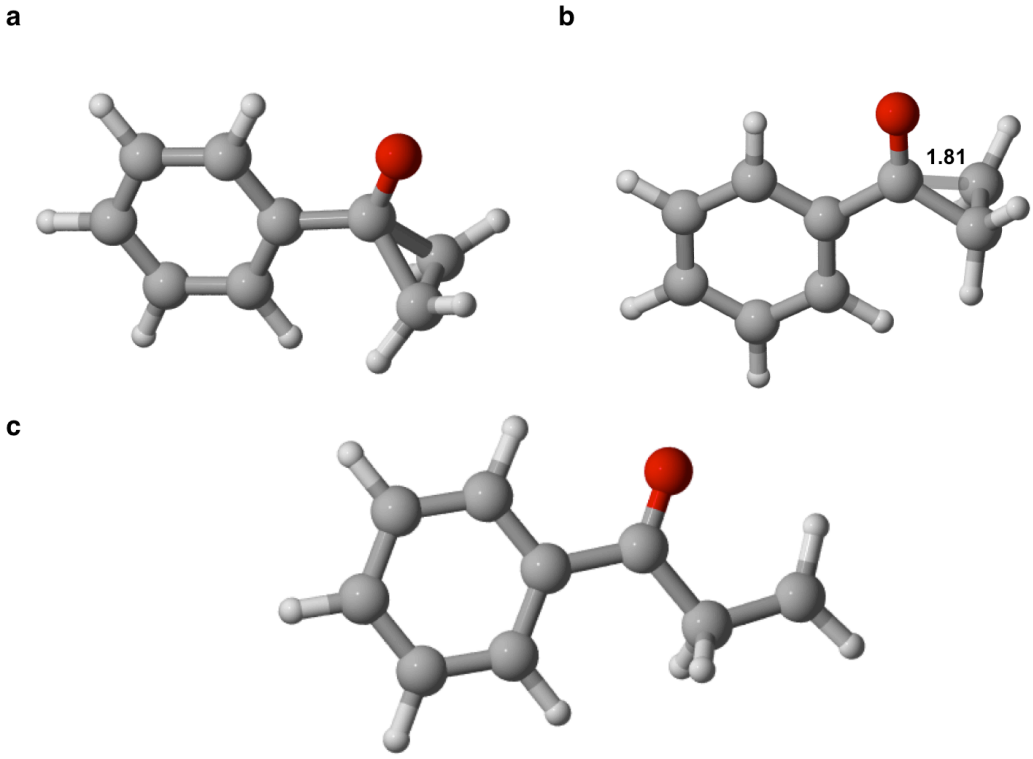


Figure 5.7 Stationary points located on the energy surface for the ring-opening of 1-Phenylcyclopropoxy radical using UM11/6-31+G** in the gas phase. a. Optimized structure for the 1-phenylcyclobutoxy radical. b. Transition state structure for the cleavage of the alkoxy radical. c. Optimized product structure of the alkyl radical generated upon the cleavage of the alkoxy radical.

The located transition state structures have exactly one imaginary frequency and starting materials and products have no imaginary frequency.

Prediction of Kinetic Isotope Effects. In order to test our hypothesis that TST cannot account for the experimental intramolecular KIEs, POLYRATE calculations were utilized. Predicted KIEs for the cleavage of 1-methylcyclobutoxy radical are summarized on **Table 5.1**.

Since TST predictions do not account for tunneling and recrossing contribution, predictions were also carried for Canonical Variational Transition State Theory[10] (CVT) with the effect of multidimenstional tunneling contribution using the Small Curvature Tunneling[68] (SCT) approximation. The prediction of small KIEs by the CVT/SCT method has the problem that tight convergence criteria and small step sizes are required for sufficient numerical convergence. However, due to the small size of the system under study the computational time was very short. These calculations were performed using GAUSSRATE[69] as the interface between POLYRATE[12] and Gaussian 09[70]. The semiclassical rate constants were computed using the Page-McIver method[71] to follow the minimum energy path (MEP) with a step size of 0.005 bohr. The predicted TST and CVT/SCT KIEs for C-3 versus C-5 were computed from the rate constants obtained from the parent calculation (all carbon atoms being ^{12}C) and calculations with a ^{13}C label at the carbon atom being broken at the transition state.

Table 5. 1 Summary of ^{13}C experimental and predicted KIEs for the cleavage of 1-Methylcyclobutoxy radical at 42 °C.

Relative Content of ^{13}C		**Experimental KIE**	
C-3	C-5	C3/C5	
1021.4	991.6407	1.030(1)	
UM11/6-31+G Predicted KIEs**			
TST	**CVT**	**TST/SCT**	**CVT/SCT**
1.049	1.048	1.058	1.058

The experimental intramolecular KIE for the cleavage of 1-methylcyclobutoxy radical does not match the predicted values from TST or CVT. While TST and CVT overestimate the intramolecular KIE, inclusion of small curvature tunneling (SCT) correction increases even more the predicted KIE. This supports our initial proposal that TST could not account for the experimental product ratio on the cleavage of alkoxy radicals.

Table 5.2 Summary of experimental and predicted intramolecular ^{13}C KIEs for the cleavage of 1-Phenylcyclopropoxy radical at 0 °C.

Relative Content of 13C		**Experimental KIE**	
C2	C3	C2/C3	
1021.4	972.7	1.050(1)	
UM11/6-31+G Predicted KIEs**			
TST	**CVT**	**TST/SCT**	**CVT/SCT**
1.038	1.037	1.041	1.039

The predicted KIE for the cleavage of 1-phenylcyclopropoxy radical, **Table 5.2**, suggests that heavy-atom tunneling does not play a crucial role on the selectivity. However, classical and quantum mechanical KIE prediction underestimate the experimental selectivity.

While predictions of the selectivity is overestimated for the cleavage of 1-methylcyclobutoxy radical and underestimated for the the cleavage of 1-phenylcyclopropoxy radical. The experimental and computational results for both systems provide no detail about the nature of the selectivity on the studied reactions, but

suggests a non-statistical behavior on these reactions. A plaussible explanation to decreased experimental selectivity in the cleavage of the four memebered ring alkoxy radical and increased experimental selectivity in the cleavage of the three membered ring when compared against computational results is presented below.

5.4 Discussion

The cleavage of alkoxy radicals was studied in order to elucidate the contribution of dynamic effects into the selectivity of this reaction. For this purpose, experimental intramolecular KIEs were measured for the product from the cleavage of 1-methyl cyclobutoxy radical, 5-chloro-2-pentanone, and the product from the cleavage of 1-phenylcyclopropoxy radical, 3-chloropropiophenone. The experimental isotope effects were compared against UM11/6-31+G** predicted KIEs using POLYRATE. Interestingly, TST and CVT predicted KIEs do not match with experimental observations. The prediction of isotope effecs was done with and without a tunneling inclusion, in order to rule out the possibility of this phenomenon playing a significant role. However, SCT correction does not predict the experimentally observed KIE. This suggests that the selectivity in the cleavage of alkoxy radicals is be susceptible to contribution from non-statistical dynamics.

The experimental KIE for the cleavage of 1-methylcyclobutoxy radical is significantly over estimated by TST and CVT. While TST and CVT predict an isotope effect of about 4.8 %, which is increased to 5.8 % by including SCT correction. The experimental KIE

is only 3 %. On the cleavage of 1-phenylcyclopropoxy radical, experimental KIE is underestimated by computational predictions. In general, the KIE is not accounted for by TST or CVT predictions. Althought, the exothermicity for the formation of the 3-membered ring alkoxy radical is greater than that of the four membered ring the selectivity in the cleavage of C-2 versus C-3 is significantly increased. Once the alkoxy radicals are formed, these intermediates that contain extra energy, must cleave in order to afford the corresponding chloroketone. As the size of the ring bearing the alkoxy radical is decrease the barrier for its cleavage is decreased or disappears as in the case for the 3-membered ring. The experimental observation of an increase in selectivity in the cleavage of 1-phenylcyclopropoxy radical is surprising to us. We would have expected that as a result of the extra energy within the alkoxy radical intermediate selectivity would decrease as we have preivourly observed on the hydroboration of alkenes and the ozonolysis of terminal alkenes.

Although, TST cannot account for the experimental KIE on the cleavage of 1-methycyclobutoxy the nature of the experimental isotope effect has not been elucidated. We propose that dynamic effects are involved on this reaction, due to the excess energy stored within these highly reactive intermediates (alkoxy radicals) or barrierless cleavage, **Figure 5.8**. While the excess energy on the cleavage of 1-methylcyclobutoxy radical decreases selectivity, the absence of a barrier shifts the nature of the selectivity on the cleavage of 1-phenylcyclopropoxy radical towards Newtonian KIEs. As a result of this, an increase in the cleavage of the lighter isotope, ^{12}C, is observed. As it was also

discussed on Chapter III, Newtonian KIEs are relatively unsensitive to temperature changes and as a result the extra energy on the cyclopropoxy radical does not affect the reaction.

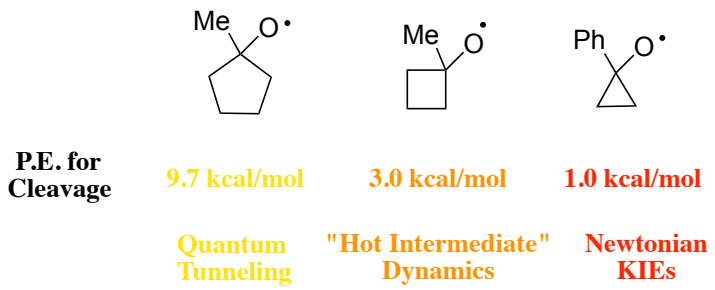


Figure 5.8 Summary of potential energy barriers by UM11/6-31+G** for the cleavage of cyclic alkoxy radicals and the proposed non-statistical behavior that controls selectivity in each case.

Further more, we also propose that cleavage of alkoxy radicals are particularly prone exhibit dynamic effects like trifurcating potential energy surfaces. The later idea is supported by the findings made by Macdonald[75,76] and colleagues on the study of the β-cleavage of decalinoxy radicals. While studying the β-cleavage of the decalinoxy radical, the formation of products from the scission of bond a, b and c were observed experimentally, **Figure 5.9**.

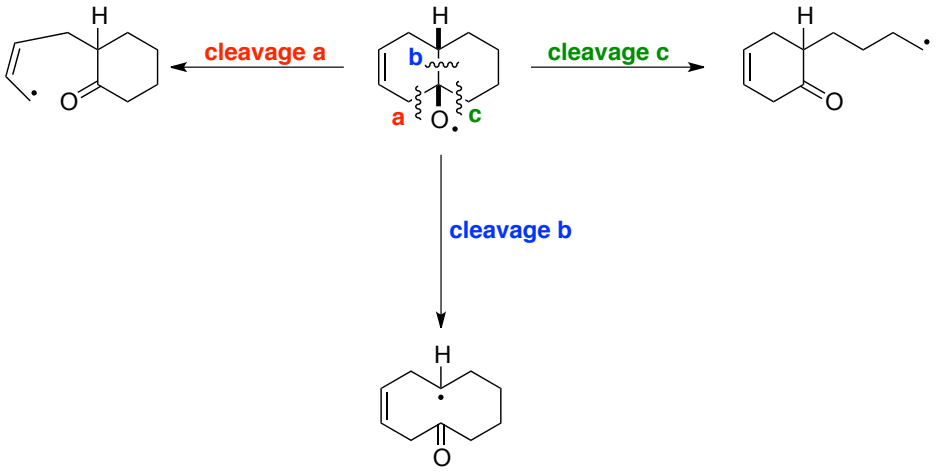


Figure 5.9 Products from the β-cleavage of decalinoxy radical at 3 cleavage sites.[75]

These results seemed surprising, since cleavage a was expected to be significantly favored over cleavage at sites b and c, due to the generation of an allylic radical. Since formation of all three products are formed from the same decalinoxy radical, we expect that this reaction is very likely to involve a trifurcating potential energy surface where a single transition state for the formation of the alkoxy radical leads to the experimentally observed products from cleavage at sites a, b and c.

Experimental observations that support the existence of a trifurcating energy surface still needs to be obtained. Also, the nature of the experimental intramolecular KIEs on the cleavage of tertiary cyclic alkoxy radicals, 1-methylcyclobutoxy, needs to be elucidated by employing computational calculations and dynamic trajectories. However, the preliminary experimental results and the proposed example to explore the possibility of a trifurcation in the potential energy surface of alkoxy radicals opens a window of

interesting possibilities to further study the role of non-statistical dynamics in the cleavage of tertiary alkoxy radicals.

CHAPTER VI

EXPLORING THE FREE ENERGY LANDSCAPES OF A DIELS-ALDER CYCLOADDITION: HIDDEN TRANSITION STATES AND ENTROPIC INTERMEDIATES. EXPERIMENTAL VS. THEORY

6.1 Introduction

The realm of pericyclic reactions encompasses a range of chemical transformations that are typically named or classified based on the characteristic features of their transition state structures. Pericyclic reactions are characterized by having a cyclic array of orbitals and proceeding via a concerted transition state. These reactions can be classified as cycloadditons, sigmatropics, electrocyclizations and cheletropic reactions, **Figure 6.1**. Although all of these are concerted reactions their transition state structures may reflect some degree of asynchronisity.

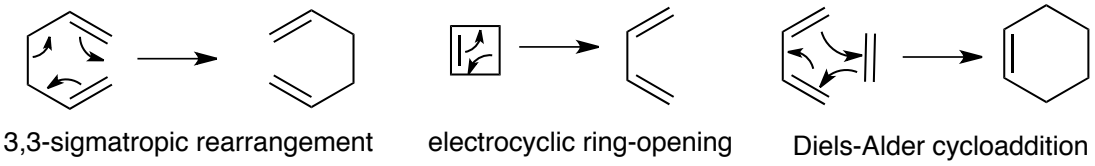


Figure 6.1 Examples of pericyclic reactions.

The Woodward-Hoffman[77-81] rules have been long used to predict whether these reactions are allowed or forbidden processes and also to understand the stereochemical outcome obtained. These rules haven proven to be powerful in the study of thermal and photochemical pericyclic reactions, however they constraint what chemists know about pericyclic reactions.

Our group has recently described a "seemingly" concerted [2+2] cycloaddition between *cis*-2-butene and dichloro ketene, **Figure 6.2**. This particular reaction seems to occur via a single step process where both bonds form in a concerted fashion when we look at the computationally predicted Potential Energy Surfarce (PES) for this reaction.

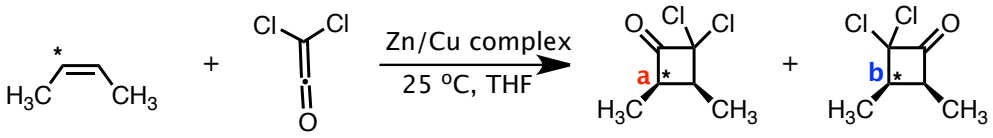


Figure 6.2 [2+2] cycloaddition between *cis*-2-butene and dichloro ketene.[23]

On the other hand when one studies the Free Energy Surface for this reaction one can observe that after a significant drop in the Free Energy along the reaction coordinate there is a slight increase in Free Energy, that makes our "seemingly" concerted reaction a two step process on a Free Energy Surface. These exciting observations had an impact on the experimental Kinectic Isotope Effects (KIEs) for the cycloaddition.

These observations have allow us to realize that by ignoring the Free Energy Surface of many ordinary organic reactions chemists miss a significant amount of interesting and important details about chemical reactions. These details can shed light about reaction mechanisms and product selectivities in situations where commonly used statistical rate theories cannot be applied. Preliminary computational results reported by James-Gonzalez, Kwan and Singleton[23] have supported that these novel mechanistic ideas are relevant in highly asynchronous Diels-Alder reactions.

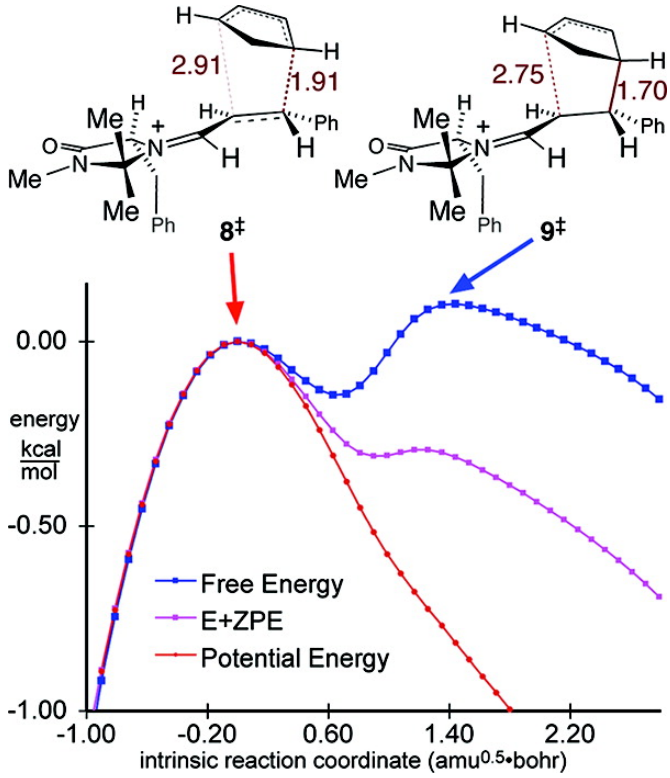


Figure 6.3 Preliminary energy profiles along IRC through transition state structure 8 for the organocatalyzed Diels-Alder reaction between cyclopentadiene and *trans*-cinnamadehyde.[23]

These preliminary results show that this reaction has two saddle points in Free Energy, but only one saddle point in potential energy surface, **Figure 6.3**. We describe here the Diels-Alder reaction between cyclopentadiene and iminium ions derived from *trans*-cinnamaldehyde. By choosing electron neutral and electron rich dienophiles we aim to study the impact on the mechanism of this imidazolidinone catalyzed Diel-Alder reaction, **Figure 6.4**. The study of this reaction was pioneered by Macmillan and co-workers as the first highly enantioselective organocatalyzed Diels-Alder reaction.[82]

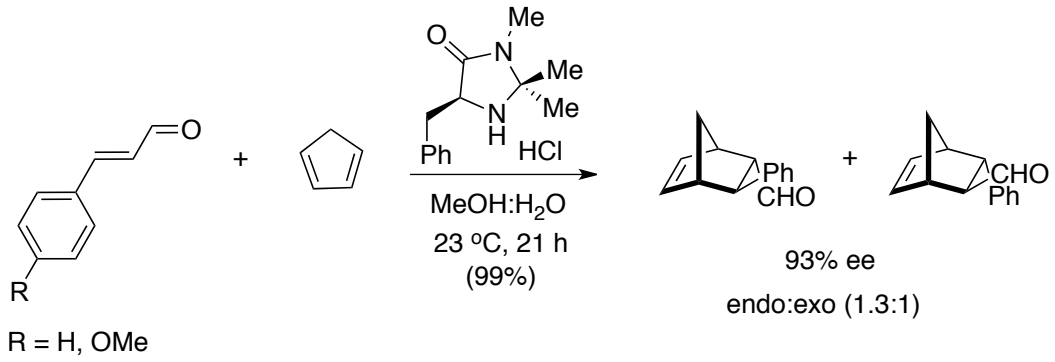


Figure 6.4 Organocatalyzed Diels-Alder reaction between cyclopentadiene and *trans*-cinnamaldehyde derivatives.

The combination of our signature NMR methodology to measure KIEs and computational studies have allow us to learn interesting details about this Diel-Alder reaction.

6.2 Experimental Results

Preparation of (1S,2S,3S,4R)-3-Phenylbicyclo[2.2.1]hept-5-ene-2-carbaldehyde and (1R,2S,3S,4S)-3-Phenylbicyclo[2.2.1]hept-5-ene-2-carbaldehyde.[82] To a solution of 0.241 g (0.95 mmol) of (5S)-5-benzyl-2,2,3-dimethylimidazolidin-4-one monohydrochloride in methanol/water (95%/5%) was added a sample of 2.38 mL (2.50 g, 18.9 mmol) of *trans*-cinnamaldehyde. The solution was stirred for 1-2 minutes before addition of 4.75 mL (3.73 g, 56.7 mmol) of fresh distilled cyclopentadiene. The reaction was stirred at room temperature for 21 hours and then diluted in diethyl ether and successively washed with water and brine. The organic layer was dried over sodium sulfate and concentrated under vacuum. The dimethylacetal formed throut the course of the reaction was hydrolyzed by stirring the crude product mixture in a 1:1:2 solution of

trifluoroacetic acid:water:chloroform at room temperature for 2 hours, followed by neutralization of the solution using sodium aqueous bicarbonate. After extracting with diethyl ether, the organic layer was dried over sodium sulfate and concentrated under vacuum. The product was purified by column chromatography using silica gel and 10% ethyl acetate in hexanes to yield 3.57 g (95 % yield) of pure endo and exo product mixture obtained as a light yellow oil. The endo:exo product ratio was calculated to be 1:1.3.

Reduction of (1S,2S,3S,4R)-3-Phenylbicyclo[2.2.1]hept-5-ene-2-carbaldehyde and (1R,2S,3S,4S)-3-Phenylbicyclo[2.2.1]hept-5-ene-2-carbaldehyde. To a solution of 2.67 g (13.5 mmol) of (1S,2S,3S,4R)-3-phenylbicyclo[2.2.1]hept-5-ene-2-carbaldehyde and (1R,2S,3S,4S)-3-phenylbicyclo[2.2.1]hept-5-ene-2-carbaldehyde in 30 mL of methanol was added 0.51 g (13.5 mmol) of sodium borohydride in small portion while cooling down the reaction mixture at 0 °C. After the addition was completed, the reaction was stirred at room temperature for an additional 30 minutes and then quenched hydrochloric acid and extracted with diethyl ether. The organic layer was dried over sodium sulfate and concentrated under vacuum. Purification was performed via column chromatography using 20% ethyl acetate in hexanes to yield 1.86 g (69 % yield) pure mixture of endo and exo alcohols as a viscous light yellow oil.

Preparation of (1S,2R,3S,4R)-3-(4-Methoxyphenyl)bicyclo[2.2.1]hept-5-ene-2-carbaldehyde and (1S,2S,3S,4R)-3-(4-Methoxyphenyl)bicyclo[2.2.1]hept-5-ene-2-carbaldehyde. To a solution of 0.784 g (3.08 mmol) of (5S)-5-benzyl-2,2,3-dimethylimidazolidin-4-one monohydrochloride in methanol/water (95%/5%) was added a sample of 10.00 g (61.1 mmol) of trans-(4-methoxy)cinnamaldehyde. The solution was stirred for 1-2 minutes before addition of 15.56 mL (12.28 g, 184.4 mmol) of fresh distilled cyclopentadiene. The reaction was stirred at room temperature for 21 hours and then diluted in diethyl ether and successively washed with water and brine. The organic layer was dried over sodium sulfate and concentrated under vacuum. The dimethylacetal formed throut the course of the reaction was hydrolyzed by stirring the crude product mixture in a 1:1:2 solution of trifluoroacetic acid:water:chloroform at room temperature for 2 hours, followed by neutralization of the solution using sodium aqueous bicarbonate. After extracting with diethyl ether, the organic layer was dried over sodium sulfate and concentrated under vacuum. The experimental endo:exo product ratio was calculated to be 1:1.4. The product was purified by column chromatography using silica gel and 10% ethyl acetate in hexanes to yield 1.58 g of 85% exo product obtained as a light yellow oil. The product obtained was subjected to sodium borohydride reduction.

Experimental Kinetic Isotope Effects. NMR samples were prepared using 300 mg of a 1.3:1 mixture of ((1S,2R,3S,4R)-3-phenylbicyclo[2.2.1]hept-5-en-2-yl)methanol and ((1S,2S,3S,4R)-3-phenylbicyclo[2.2.1]hept-5-en-2-yl)methanol or 300 mg of 85 % ((1*S*,2*S*,3*S*,4*R*)-3-(4-methoxyphenyl)bicyclo[2.2.1]hept-5-en-2-yl)methanol in 5 mm

NMR tubes filled to a constant height of 5 cm with $CDCl_3$. The ^{13}C spectra were recorded at 125.81 MHz using inverse gated decoupling, delays of 10 s between $\pi/2$ calibrated pulses and a 5 s acquisition time to collect 312,500 points. Integrations were numerically determined using a constant integration region for each peak that was a constant multiple of the peak widths at half-height. In accordance with the methodology we have previously published, for the integration of each pair of corresponding positions within the endo:exo mixture or exo alcohol the transmitter was set half way in between the two peaks of interest on each measurement.[5] A zero-order baseline correction was generally applied, but to avoid any qualitative manipulation no first-order or higher-order baseline correction was ever applied. Six spectra were recorded on each sample. The assignment of the peaks in the ^{13}C spectrum of alcohols mixture was performed using a combination of 2-D NMR experiments (COSY, HMBC and HSQC).

The experimental intramolecular KIEs for the organocatalyzed Diels-Alder reaction were measured for two independently prepared samples of the endo:exo alcohol and two independently prepared samples of 85% exo alcohol after sodium borohydride reduction. The experimental intramolecular KIEs are summarized in **Figure 6.5**. In general, the intramolecular KIEs reflect the asyncronisity of the TS for the cycloaddition. The experimental KIEs on the endo:exo alcohols prepared from the parent aldehyde, *trans*-cinnamaldehyde, are about the same magnitude. Also, an inverse KIE on the exo 4-methoxy alcohol is 3 %, which suggests a late TS with C-C bond **a** significantly more

advanced than C-C **b**. The mechanistic implications or suggestions of the experimental intramolecular KIEs will be discussed on the next section along with the predicted KIEs.

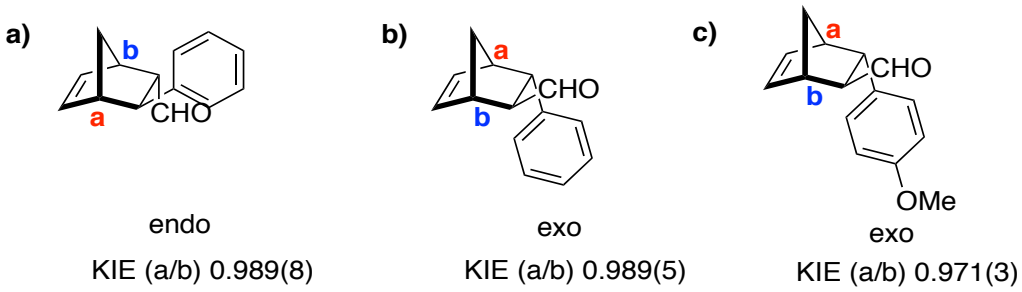


Figure 6.5 Experimental Intramolecular KIE for iminium catalyzed Diels-Alder reaction measured on $CDCl_3$. The 95% confidence interval is shown in parenthesis for each value. KIEs from a and b were measured simultaneously from a 1.3:1 endo:exo mixture. The KIE on c was measured from an 85% pure exo cycloadduct.

6.3 Computational Results

Choosing the Optimal Method and Basis Set. Computational studies for the organocatalyzed Diels-Alder reaction between cyclopentadiene and *trans*-cinnamaldehyde were performed using B3LYP/6-31G* gas phase calculations. The choice of this method and basis set was made based on preliminary results published in the Singleton Group. Although of the limitations of the B3LYP method to study Diels-Alder reactions, DFT methods over estimate the energy of pi bonds compared to sigma bonds, preliminary calculations showed interesting preliminary observations that suggested dynamically controlled reaction selectivity. The Energy surface for the cycloaddition between cyclopentadiene with *trans*-cinnamaldehyde and with *p*-methoxy *trans*-cinnamaldehyde. The corresponding located transition state structures for the formation of endo cycloadducts have only one imaginary frequency and are shown on

Figure 6.6. Both structures reveal a highly asynchronous transition state, with the C-C bond next to the phenyl ring more advanced.

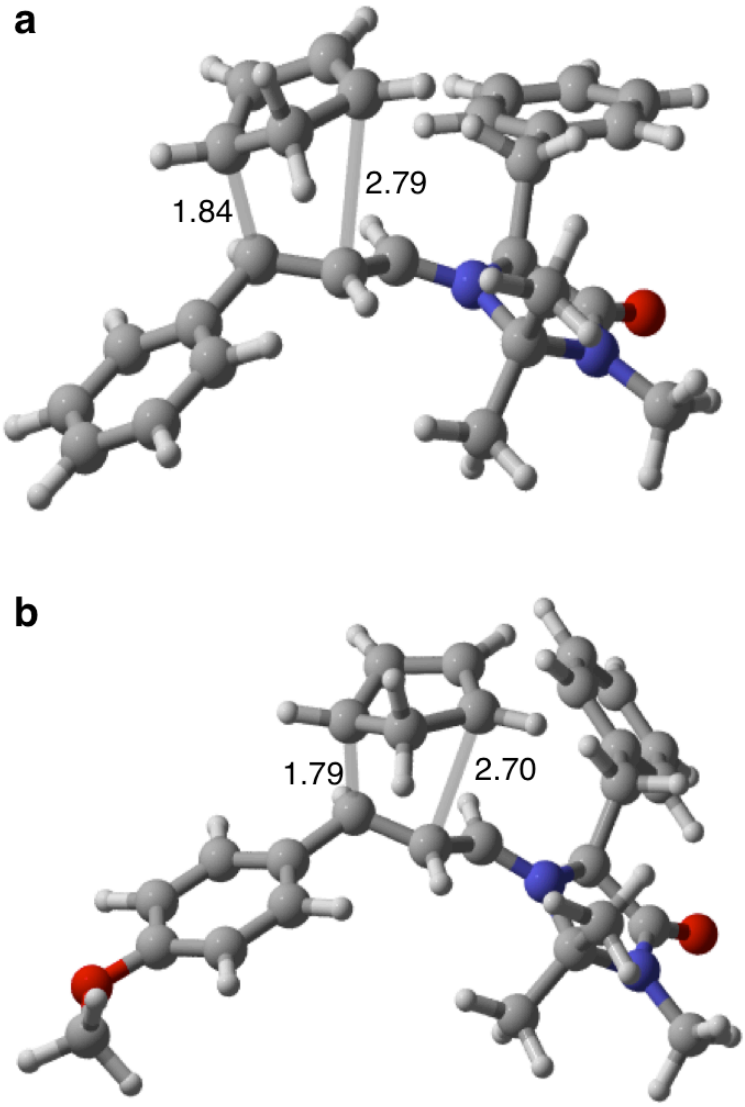


Figure 6.6 B3LYP/6-31G* gas phase Transition state structures for the Macmillan organocatatalyzed Diels-Alder reaction leading to the endo cycloadduct. a. Transition state structure for the cycloaddition between cyclopentadiene and the parent *trans*-cinnamaldehyde. b. Transition state structure for the reaction between cyclopentadiene and *trans*-4-(methoxy)cinnamaldehyde.

The transition state structure for the formation of the exo-cycloadduct from the reaction between cyclopentadiene and *trans*-4-(methoxy)cinnamaldehyde was also located, **Figure 6.7**.

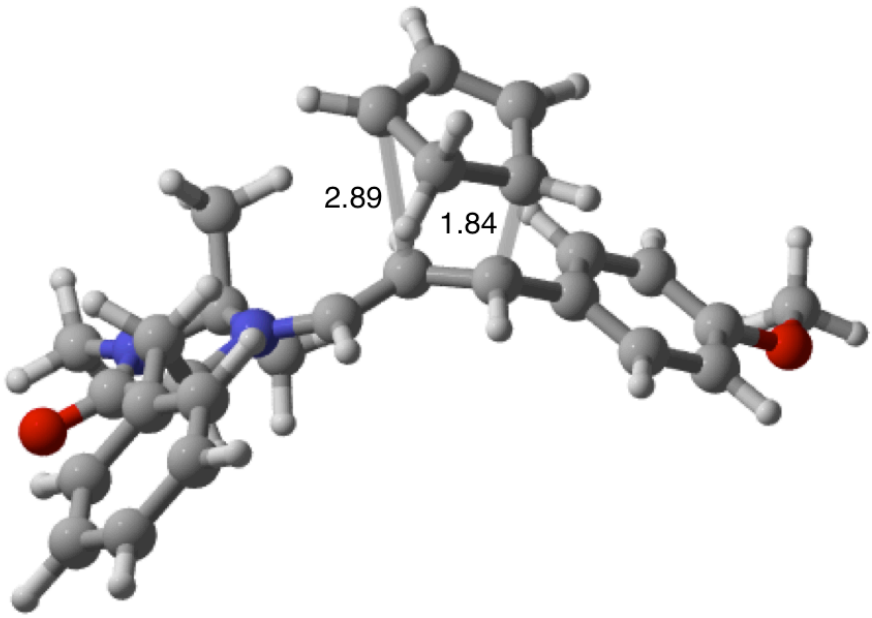


Figure 6.7 B3LYP/6-31G* gas phase transition state structure for the cycloaddition between cyclopentadiene and *trans*-4-(methoxy)cinnamaldehyde for the formation of the exo-cycloadduct.

This transition structure is also highly asynchronous but is slightly later than the transition state corresponding to the formation of the endo-cycloadduct. Due to the high asyncronisity we expected that this reaction could be susceptible to a significant amount of non-statistical recrossing, leading to an inverse intramolecular KIE. In addition, based on preliminary results we expected to observe hidden details on the Free Energy surface for this reaction that could shed light about the mechanisms of this reaction.

Exploring the Free Energy Landscapes. In order to explore the Free Energy surface for this reaction, Polyrate calculations were performed. **Figure 6.8** illustrates the free-energy profile starting from the transition state structure for the cycloadditon between cyclopentadiene and *trans*-4-(methoxy)cinnamaldehyde to yield the endo cycloadduct.

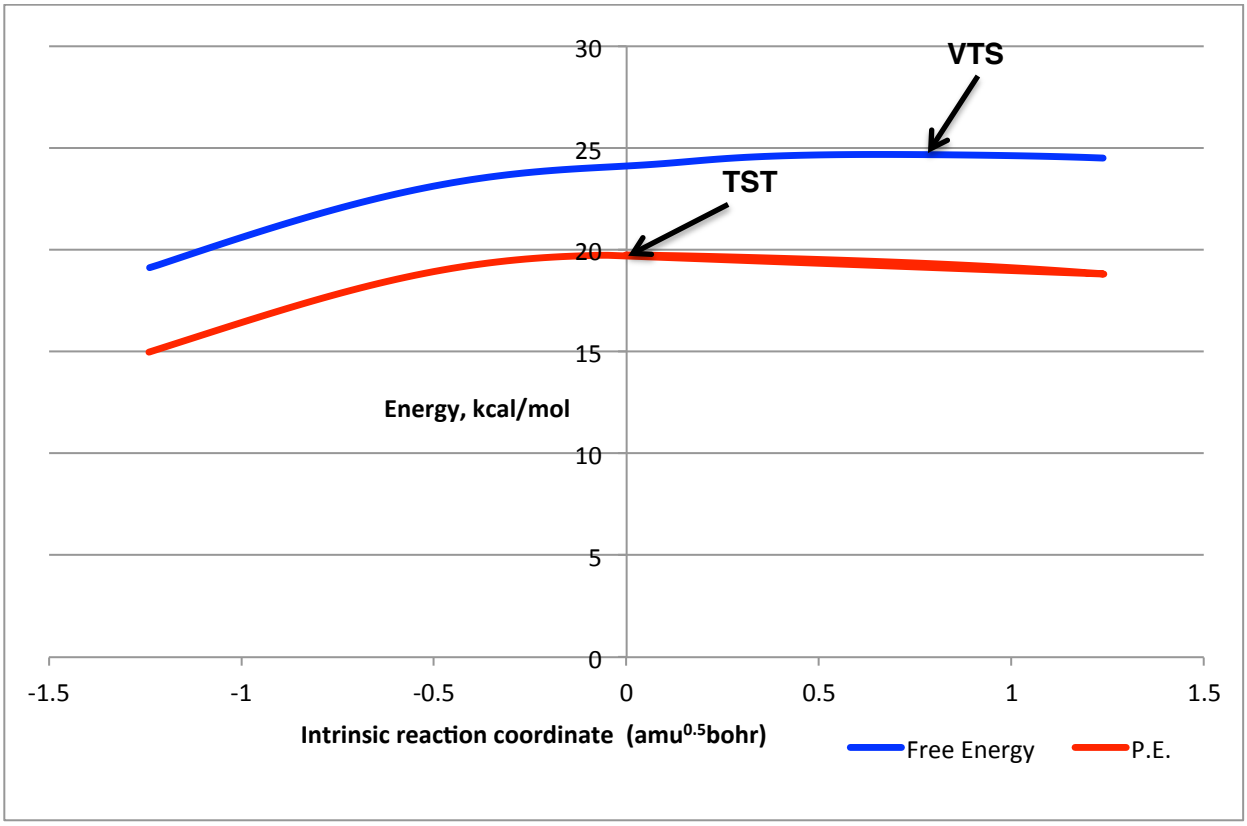


Figure 6.8 Energy profile along the IRC through transition state structure for the Diels-Alder cycloaddition between cyclopentadiene and *trans*-4-(methoxy)cinnamaldehyde to afford the endo product. The free-enrgy profile is based on generalized free energies of activation obtained from GAUSSRATE.[69]

The energy profile shows that there is a significant difference in the location of the conventional tradition state (TST) and the variational transition state (VTS). A very similar energy profile is also observed for the exo cycloadduct.

Because the conventional transition state is place at position different than at the maximum in free energy, it does not account for non-statistical recrossing. This could lead to unusual KIEs that cannot be accounted for by TST. In addition, the high asyncronisity of the cycloaddition can also impact these KIEs. To gauge our hypothesis we predicted the KIEs for the formation of endo and exo cycloadducts from their corresponding transition state structures.

Computationally Predicted KIEs. Predicted KIEs were generated using QUIVER[11] from the scaled theoretical vibrational frequencies by the method of Biegeleisen and Mayer. The predicted isotope effects reflect the preference for ^{12}C or ^{13}C at a position, a or b, in the bridgeheads of the product from the reaction for the parent system (**Figure 6.9 a and b**) and for the exo cycloadduct on 4-(methoxy)-cinnamaldehyde (**Figure 6.9 c**).

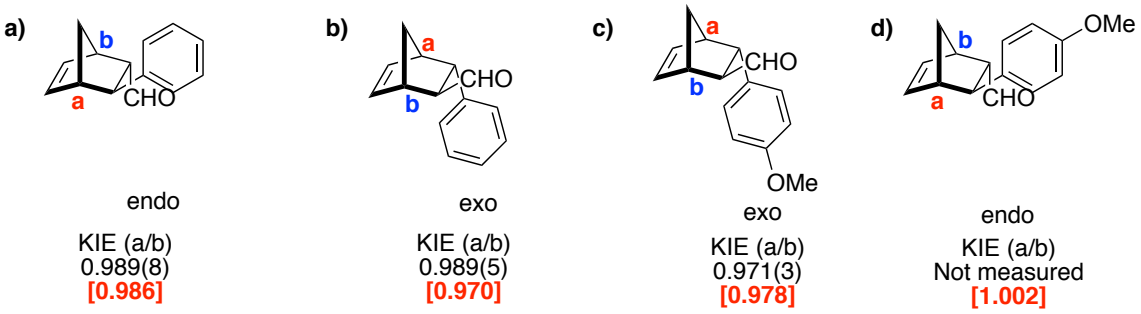


Figure 6.9 B3LYP/6-31G* predicted intramolecular KIEs for endo and exo cycloaddition products on the gas phase. Numbers on black are experimental KIEs and numbers in red are computational predictions of KIEs.

B3LYP/6-31G* predictions of the isotope effects reflect a 0.2 % preference for ^{13}C to be on the bridgehead labeled as a, more advanced bond at the transition state, of the endo product (**Figure 6.9 d**). KIE prediction for the exo product is a normal isotope effect with 2% preference for more ^{12}C to be on the more advanced C-C bond. The predicted KIEs for the two products are opposite in trend reflecting two different energy surfaces and mechanistic pictures for the formation of both products.

6.4 Discussion

Switching from the parent *trans*-cinnamaldehyde dienophile to the less reactive *trans*-4-(methoxy)cinnamaldehyde a decreased on the exothermicity of the overall cycloaddition that would result on a looser transition state structure and thus on an increased amount of recrossing. The experience gained while studying this system, has lead to hypothesize some elements that might be crucial for the experimental detection of an entropic intermediate. Reactions with a low enthalpic barrier are good candidates to exhibit experimental entropic intermediates, since in highly exothermic reactions molecules will have no time to make a choice between a pair of isotopomers while reacting. A loose transition state are also crucial, since this would increase the amount of non-statistical recrossing for reactions and to an initial increase on the entropy of activation for a reaction, followed by a drop in entropy as the molecules on transition state approach the product channel.

Although some questions remain unsolved regarding the contribution of dynamic effects on these reactions, it is important to recognize the limitations of B3LYP as a functional to evaluate reactions that involve bonding changes from pi (π) to sigma (σ) bonds. B3LYP underestimates the energy of sigma (σ) bonds, leading computational predictions to estimate an exceedingly large amount of non-statistical recrossing. The inaccuracy of the computational method employed to study the energy surface in predicting non-statistical recrossing on the organocatalyzed Diels-Alder reactions is shown by the reasonably good agreement between experimental intramolecular KIEs and the TST predicted KIES using B3LYP/6-31G*.

CHAPTER VII

CONCLUSIONS

Intramolecular KIEs at natural abundance using NMR methodology have been measured for a series of organic reactions in order to elucidate the contribution of dynamic effects on their selectivity. Intramolecular KIEs are measured when symmetrical starting materials break an element of symmetry to afford products of lower symmetry. Intramolecular KIEs provide details about the product-determing step in chemical reactions. Experimental KIEs were combined with dynamic trajectories and other computational calculations in order to elucidate fine mechanistich details about the reactions under study.

The surprising existence of isotope effects in the dimerization of methacrolein was studied. The origin of intramolecular isotope effects on the methacrolein dimer has been stablished in classical physics, in Newton's second law, rather than quantum mechanics, tunneling and/or ZPE. This was accomplished by employing quasiclassical and classical dynamic trajectories utilizing "super-heavy" carbon atoms. Results from both set of dynamic trajectories were statistically indistinguishable, leading to the conclusion that ZPE has very little or no contribution in the origin of the isotope effects. Following the desymmetrization along the minimum energy path (IRC) by including a heavy atom at one of the positions, atomic motion reaction coordinate diagrams were generated to illustrate the qualitative idea that controls the selectivity in the product formation.

Because TST cannot account for the experimental product ratio, we have identified Newtonian isotope effects as the selectivity control for this reation.

The dimerization of cyclopentadienone constitutes a great system to study the temperature effect in Newtonian isotope effects. The experimental intramolecular KIEs were measured for dicyclopentadienone prepared at 195 K and 298 K. The KIEs for the dimer at both temperatures were the same within experimental error and quasiclassical dynamic trajectories at these temperatures showed that KIEs are relatively temperature independent within a 100 degrees range. Predicted intramolecular KIEs follow the same trend as experimental results. Extrapolated KIE is in good agreement with experimental isotope effects.

The cleavage of alkoxy radicals is of great interest to us since these highly reactive intermediates are formed with excess energy, making their cleavage prone to be behave in a non-statistical fashion. The contribution of quantum mechanical tunneling in the cleavage of 1-methylcyclopentoxy radical was revealed by combining the experimental intramolecular KIEs with POLYRATE calculations. Although heavy atom tunneling contribution into the KIE for the cleavage of 1-methylcyclopentoxy radical is small, TST underestimates the experimental KIE by not accounting for such phenomenon. The cleavage of 1-methylcyclopentoxy radical exhibits heavy-atom tunneling at en elevated temperature, illustrating the idea that tunneling is present in every reaction and it is traceable only in those reactions where its contribution is large enough to be detected.

The more reactive 1-methylcyclobutoxy and 1-phenylcyclopropoxy radicals have lower cleavage barriers, what could result in a large deviation from a statistical behavior. Experimental intramolecular KIEs for the chloroketone obtained as the product from the cleavage of the corresponding alkoxy radicals, are not in agreement with those predicted by TST and CVT using POLYRATE calculations. Although the origin of these KIEs has not been stablished, dynamic effects seem to contribute to the experimentally observed isotope effects.

Preliminary computational results suggested that iminium catalyzed Diels-Alder reaction between cyclopentadiene and *trans*-cinnamaldehyde could potentially involve dynamic effects. While computational calculations predicted that this "seemingly" concerted cycloaddition was likely to exhibit a large amount of non-statistical recrossing, experimental intramolecular KIEs match to some extent with those predicted by TST. The reason for the discrepancy between computational expectations and experimental KIEs is attributed to the limitations of B3LYP to underestimate the strength of sigma bonds, that results in an increased amount of transition state recrossing.

In conclusion, a combination of experimental intramolecular KIEs and computational calculations has been applied to study a series of ordinary organic reactions. Both techniques when applied in conjunction have proven to accurate in the elucidation of mechanistic details in chemical reactions.

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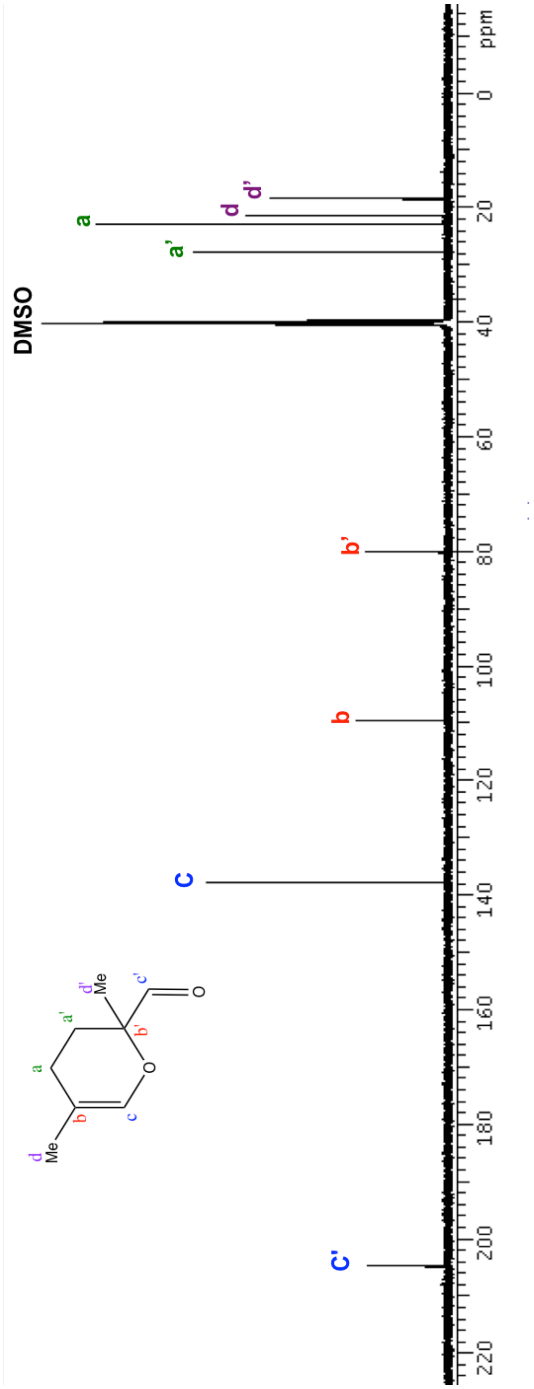
APPENDIX A

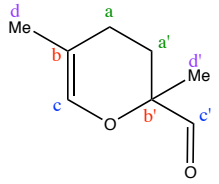
NMR DATA

A.1 ^{13}C NMR assignment of Methacrolein dimer



A.2 ^{13}C NMR raw integrations for Methacrolein dimerization

The letters on the figure below depict the pairs of competing diene/dienophile atoms in the ^{13}C NMR spectrum of a concentrated sample. The integrations in the table below are given in this order. The numbers provided are taken from a total of 48 spectra, arising from 6 spectra for each competing position of two independently prepared samples.



Sample 1

Table of Results for Carbon a versus a'

	a	a'
fid 1	100.00	98.82
fid2	100.00	98.80
fid 3	100.32	98.80
fid 4	99.86	98.99
fid 5	100.01	98.70
fid 6	100.00	98.82

Table of Results for Carbon b versus b'

	b	b'
fid 1	100.00	98.00
fid2	99.67	97.93
fid 3	99.39	98.04
fid 4	99.49	98.25
fid 5	99.34	97.81
fid 6	99.48	97.92

Table of Results for Carbon c versus c'

	c	c'
fid 1	99.05	100.00
fid2	98.85	99.68
fid 3	99.04	99.49
fid 4	98.89	99.57
fid 5	98.88	99.39
fid 6	98.90	99.58

Table of Results for Carbon d versus d'

	d	d'
fid 1	100.00	100.02
fid2	99.88	100.07
fid 3	100.00	99.89
fid 4	99.91	99.88
fid 5	99.74	99.97
fid 6	99.98	99.97

Sample 2

Table of Results for Carbon a versus a'

	a	a'
fid 1	100.00	99.37
fid2	100.26	99.28
fid 3	100.34	99.80
fid 4	100.17	99.56
fid 5	100.62	99.28
fid 6	100.45	99.06

Table of Results for Carbon b versus b'

	b	b'
fid 1	100.00	97.69
fid2	99.73	97.80
fid 3	99.49	97.30
fid 4	99.22	97.04
fid 5	99.09	97.14
fid 6	99.11	97.33

Table of Results for Carbon c versus c'

	c	c'
fid 1	99.36	100.00
fid2	100.06	100.58
fid 3	100.13	100.38
fid 4	99.68	100.31
fid 5	99.69	100.14
fid 6	99.13	99.65

Table of Results for Carbon d versus d'

	d	d'
fid 1	100.00	100.56
fid2	100.00	100.15
fid 3	99.98	100.06
fid 4	99.77	99.97
fid 5	99.43	100.02
fid 6	99.85	99.74

A.3 ^{13}C Peak ratios for individual samples of methacrolein dimer

For each of the 48 spectra, simple peak ratios were calculated for the pair of peaks arising from competing positions. These ratios, their average values, and standard deviations are given in the table below. The particular peak ratios taken are given in the left-hand column.

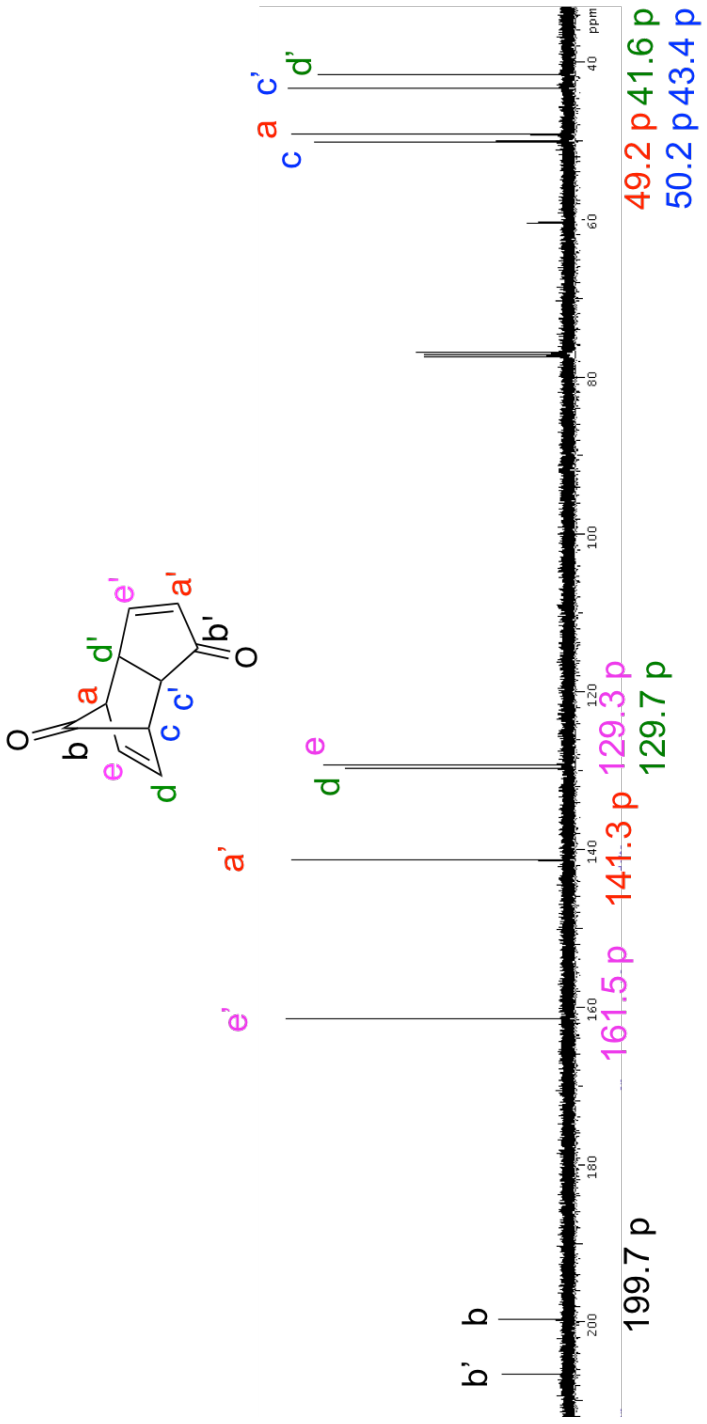
Sample 1

	fid 1	fid 2	fid 3	fid 4	fid 5	fid 6	Average	Stdev
a/a'	1.0119	1.0121	1.0154	1.0088	1.0133	1.0119	1.0122	0.0021
b/b'	1.0204	1.0178	1.0138	1.0126	1.0156	1.0159	1.0160	0.0028
c/c'	0.9905	0.9917	0.9955	0.9932	0.9949	0.9932	0.9931	0.0019
d/d'	0.9998	0.9981	1.0011	1.0003	0.9977	1.0001	0.9995	0.0013

Sample 2

	fid 1	fid 2	fid 3	fid 4	fid 5	fid 6	Average	Stdev
a/a'	1.0063	1.0099	1.0054	1.0061	1.0135	1.0140	1.0092	0.0039
b/b'	1.0236	1.0197	1.0225	1.0225	1.0201	1.0211	1.0216	0.0015
c/c'	0.9936	0.9948	0.9975	0.9937	0.9955	0.9948	0.9950	0.0014
d/d'	0.9944	0.9985	0.9992	0.9980	0.9941	1.0011	0.9976	0.0028

A.4 ^{13}C NMR assignment of Dicyclopentadienone.



A.5 ^{13}C NMR raw integrations for dicyclopentadienone prepared at 195 K.

Sample 1

	a	a'
fid 1	1000	1021.179258
fid 2	1000	1018.869462
fid 3	1000	1021.429593
fid 4	1000	1021.429593
fid 5	1000	1020.387339
fid 6	1000	1020.824826

Sample 2

	a	a'
fid 1	1000	1018.37
fid 2	1000	1015.07
fid 3	1000	1020.15
fid 4	1000	1016.91
fid 5	1000	1020.79
fid 6	1000	1018.43

Sample 1

	b	b'
fid 1	1000	1008.12
fid 2	1000	1006.72
fid 3	1000	1014.74
fid 4	1000	1001.70
fid 5	1000	999.31
fid 6	1000	1002.62

Sample 2

	b	b'
fid 1	1000	1009.80
fid 2	1000	1009.80
fid 3	1000	1004.4
fid 4	1000	1005.38
fid 5	1000	1003.17
fid 6	1000	1004.17

Sample 1

	c'	c
fid 1	987.41	1000
fid 2	991.52	1000
fid 3	988.10	1000
fid 4	986.55	1000
fid 5	990.08	1000
fid 6	987.59	1000

Sample 2

	c'	c
fid 1	985.77	1000
fid 2	985.21	1000
fid 3	985.80	1000
fid 4	980.93	1000
fid 5	986.78	1000
fid 6	983.73	1000

A.6 ^{13}C NMR raw integrations for dicyclopentadienone prepared at 298 K.

Sample 1

	a	a'
fid 1	1000	1021.92
fid 2	1000	1025.66
fid 3	1000	1027.25
fid 4	1000	1017.41
fid 5	1000	1022.79
fid 6	1000	1021.57

Sample 2

	a	a'
fid 1	1000	1022.56
fid 2	1000	1026.53
fid 3	1000	1026.09
fid 4	1000	1030.62
fid 5	1000	1021.5
fid 6	1000	1031.36

Sample 1

	b	b'
fid 1	1000	999.67
fid 2	1000	1001.49
fid 3	1000	1004.51
fid 4	1000	1001.54
fid 5	1000	1001.45
fid 6	1000	1010.99

Sample 1

	c	c'
fid 1	1000	989.99
fid 2	1000	989.77
fid 3	1000	990.01
fid 4	1000	992.65
fid 5	1000	1004.12
fid 6	1000	1002.6

Sample 2

	c	c'
fid 1	1000	984.58
fid 2	1000	994.52
fid 3	1000	991.14
fid 4	1000	994.08
fid 5	1000	992.98
fid 6	1000	991.42

A.7 ^{13}C NMR raw data integrations for Dicylopentadienone equilibration

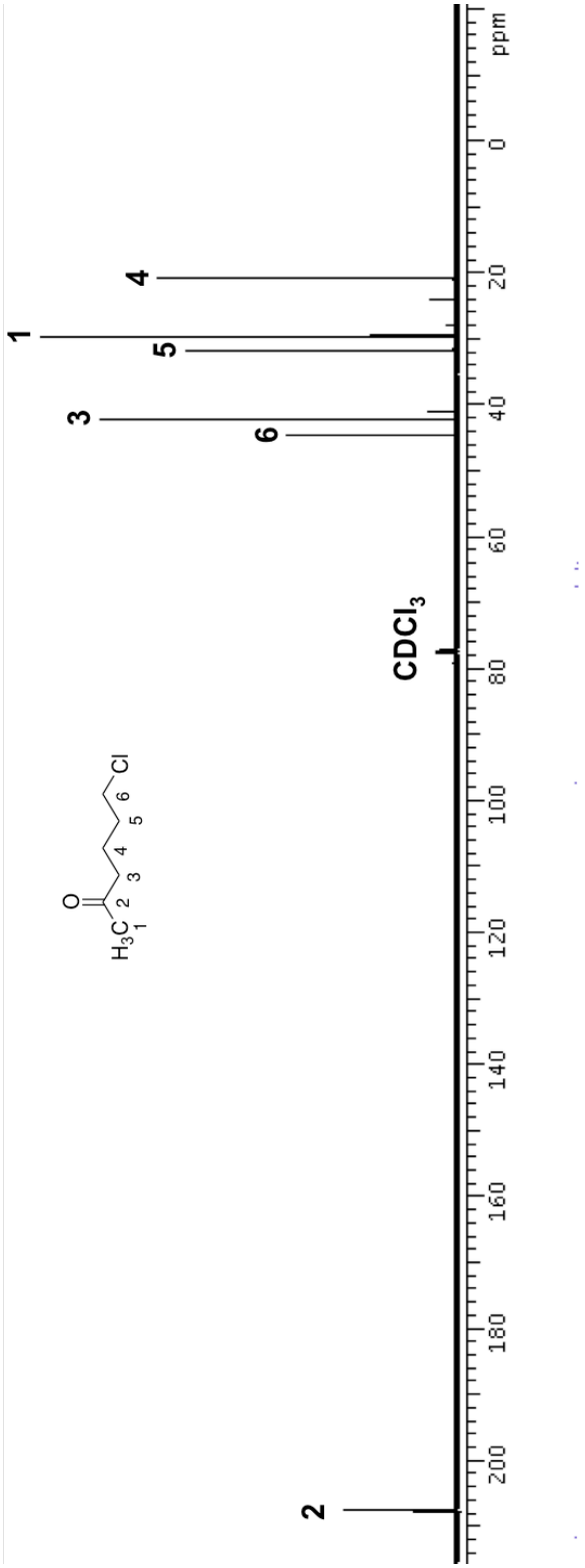
Equlibration time 1hr

	a	a'
fid 1	97.6	100
fid 2	98.03	100
fid 3	97.55	100
fid 4	97.64	100
fid 5	97.92	100
fid 6	98.32	100

Equlibration time 2hr

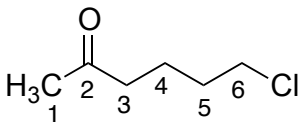
	a	a'
fid 1	100	101.10
fid 2	100	100.25
fid 3	100	100.61
fid 4	100	100.94
fid 5	100	100.62
fid 6	100	100.58

A.8 ^{13}C NMR assingment for 6-Chloro-2-hexanone



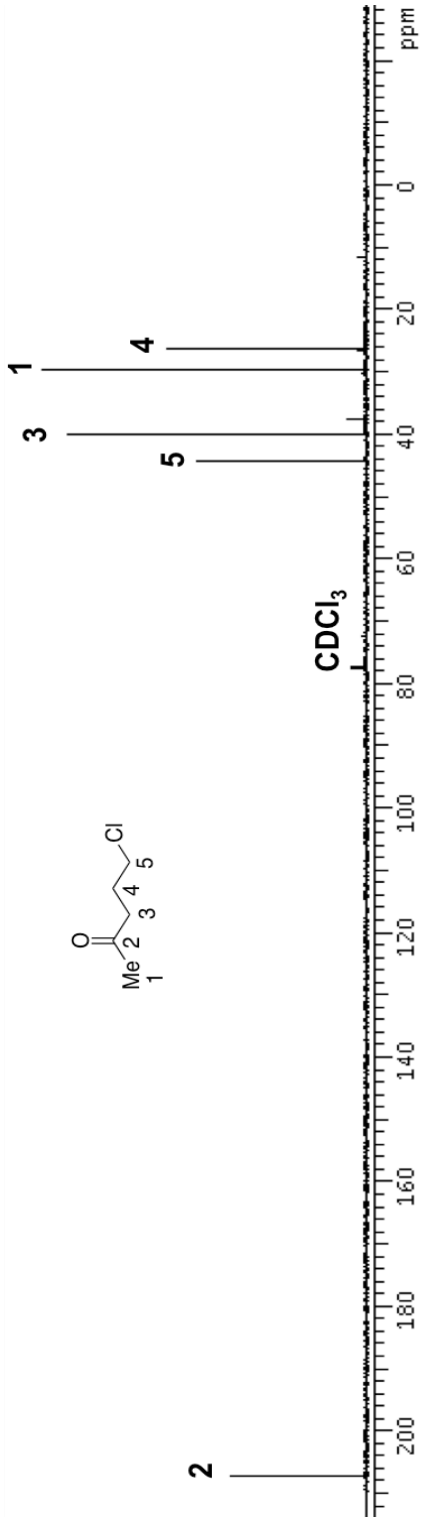
A.9 ^{13}C NMR raw integrations for 6-Chloro-2-hexanone

The number on the figure below depict the pair of competing atoms cleavage of C3 versus cleavage of C6 in the ^{13}C NMR spectrum of a concentrated sample. The integrations in the table below are given in this order. The numbers provided are taken from a total of 12 spectra, arising from 6 spectra for each competing position of two independently prepared samples.



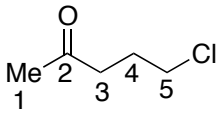
Sample 1			Sample 2		
	C3	C6		C3	C6
fid 1	1000	960.57	fid 1	1000	963.48
fid 2	1000	965.04	fid 2	1000	956.90
fid 3	1000	962.47	fid 3	1000	961.02
fid 4	1000	970.46	fid 4	1000	960.98
fid 5	1000	965.28	fid 5	1000	962.30
fid 6	1000	967.70	fid 6	1000	964.14

A.10 ^{13}C NMR assingment for 5-Chloro-2-pentanone



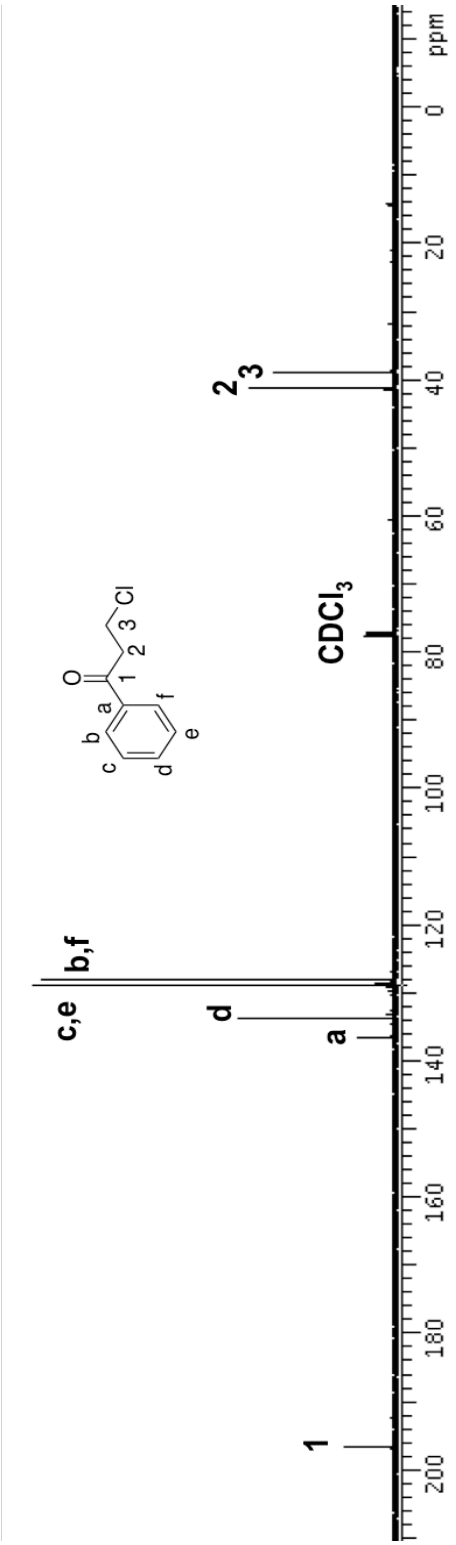
A.11 ^{13}C NMR raw integrations for 5-Chloro-2-pentanone

The number on the figure below depict the pair of competing atoms cleavage of C3 versus cleavage of C5 in the ^{13}C NMR spectrum of a concentrated sample. The integrations in the table below are given in this order. The numbers provided are taken from a total of 16 spectra, arising from 8 spectra for each competing position of two independently prepared samples.



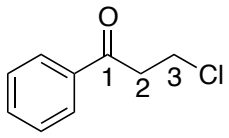
Sample 1			Sample 2		
	C5	C3		C5	C3
fid 1	980.57	1000	fid 1	982.54	1000
fid 2	980.69	1000	fid 2	982.98	1000
fid 3	981.64	1000	fid 3	982.17	1000
fid 4	981.91	1000	fid 4	983.73	1000
fid 5	980.15	1000	fid 5	982.94	1000
fid 6	979.43	1000	fid 6	983.22	1000
fid 7	974.14	1000	fid 7	982.03	1000
fid 8	978.87	1000	fid 8	981.27	1000

A.12 ^{13}C NMR assignment for 3-Chloropropiophenone



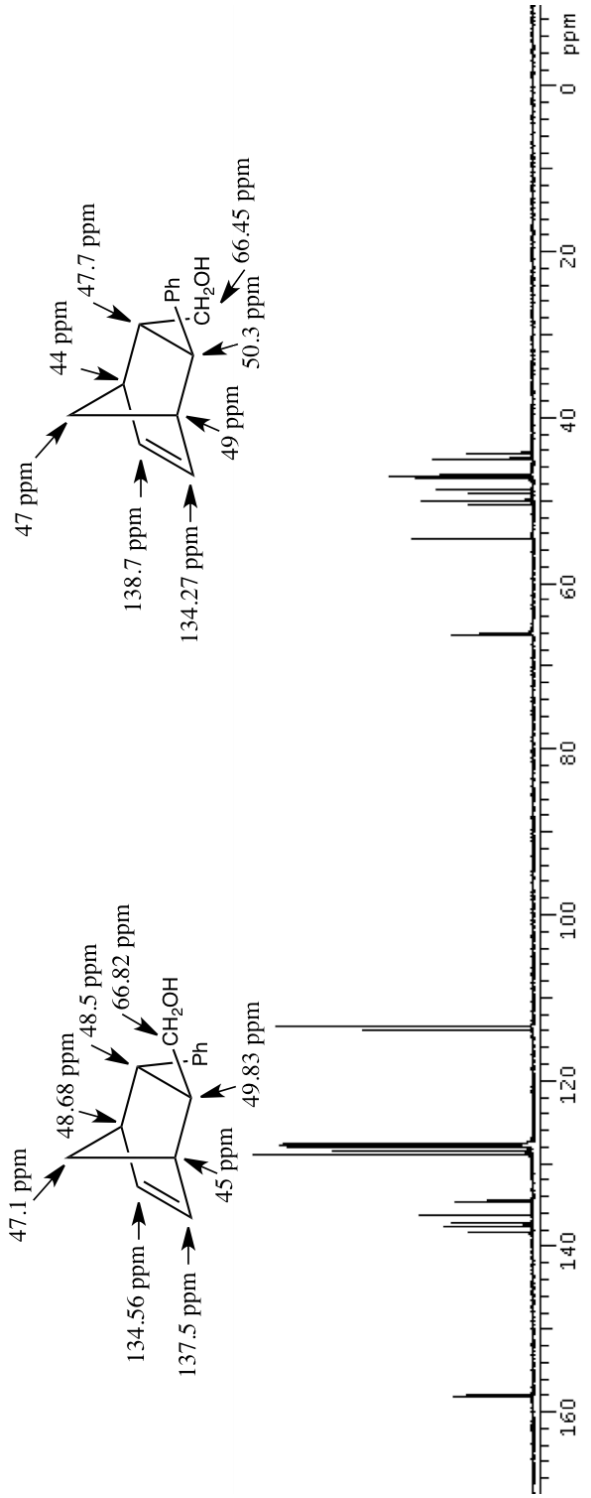
A.13 ^{13}C NMR raw integrations for 3-Chloropropiophenone

The number on the figure below depict the pair of competing atoms cleavage of C2 versus cleavage of C3 in the ^{13}C NMR spectrum of a concentrated sample. The integrations in the table below are given in this order. The numbers provided are taken from a total of 12 spectra, arising from 6 spectra for each competing position of two independently prepared samples.



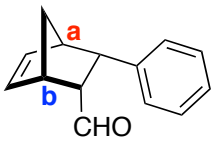
Sample 1			Sample 2		
	C2	C3		C2	C3
fid 1	1000	961.51	fid 1	1000	963.82
fid 2	1000	964.79	fid 2	1000	957.35
fid 3	1000	963.13	fid 3	1000	960.77
fid 4	1000	960.99	fid 4	1000	963.57
fid 5	1000	962.91	fid 5	1000	962.72
fid 6	1000	960.51	fid 6	1000	963.82

A.14 ^{13}C NMR assignment for ((1S,2R,3S,4R)-3-Phenylbicyclo[2.2.1]hept-5-en-2-yl)methanol and ((1S,2S,3S,4R)-3-Phenylbicyclo[2.2.1]hept-5-en-2-yl)methanol

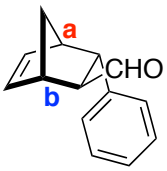


A.15 ^{13}C NMR raw integrations for (1S,2S,3S,4R)-3-Phenylbicyclo[2.2.1]hept-5-ene-2-carbaldehyde and (1R,2S,3S,4S)-3-Phenylbicyclo[2.2.1]hept-5-ene-2-carbaldehyde

The letters on the figure below depict the pair of competing C-C bonds in the ^{13}C NMR spectrum of a concentrated sample. The integrations in the table below are given in this order. The numbers provided are taken from a total of 12 spectra, arising from 6 spectra for each competing position of two independently prepared samples.



endo



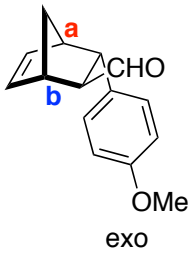
exo

Sample 1	Endo	Exo	Exo	Endo
	a	a	b	b
	44 ppm	**45 ppm**	**48 ppm**	**49 ppm**
fid 1	100	135.937	133.575	100.096
fid 2	100	135.224	133.5	99.3545
fid 3	100	135.883	133.591	99.6982
fid 4	100	134.864	132.543	99.279
fid 5	100	135.376	133.332	99.5058
fid 6	100	135.525	133.406	99.6022

Sample 2	Endo	Exo	Exo	Endo
	a	a	b	b
	44 ppm	**45 ppm**	**48 ppm**	**49 ppm**
fid 1	100	124.83	124.31	98.94
fid 2	100	124.55	124.22	98.29
fid 3	100	124.88	124.19	98.76
fid 4	100	124.58	123.44	98.35
fid 5	100	124.74	123.44	97.69
fid 6	100	124.55	123.3	97.76

A.16 ^{13}C NMR raw data for (1S,2S,3S,4R)-3-Phenylbicyclo[2.2.1]hept-5-ene-2-carbaldehyde

The letters on the figure below depict the pair of competing C-C bonds in the ^{13}C NMR spectrum of a concentrated sample. The integrations in the table below are given in this order. The numbers provided are taken from a total of 12 spectra, arising from 6 spectra for each competing position of two independently prepared samples.



exo

Sample 1	Exo		Sample 2	Exo	
	a	b		a	b
	48.7ppm	**45 ppm**		**48.7ppm**	**45 ppm**
fid 1	1000	1030.29	fid 1	1000	1031.74
fid 2	1000	1030.48	fid 2	1000	1032.8
fid 3	1000	1028.4	fid 3	1000	1024.37
fid 4	1000	1026.47	fid 4	1000	1030.21
fid 5	1000	1027.05	fid 5	1000	1034.64
fid 6	1000	1030.5	fid 6	1000	1031.83

APPENDIX B

STRUCTURES, ENERGIES AND COMPUTATIONAL PROGRAMS

B.1 Located structures and energies for the dimerization of methacrolein

Transition Structures for dimerization of Methacrolein

B3PW91/6-31G*
E(RB3PW91) = -462.258583938

Zero-point correction= 0.182750 (Hartree/Particle)
Thermal correction to Energy= 0.194062
Thermal correction to Enthalpy= 0.195006
Thermal correction to Gibbs Free Energy= 0.146648
Sum of electronic and ZPE= -462.075834
Sum of electronic and thermal Energies= -462.064522
Sum of electronic and thermal Enthalpies= -462.063578
Sum of electronic and thermal Free Energies= -462.111936

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	121.776	40.255	101.777

C,0,0.0166513371,-0.0470571695,0.0076390864
C,0,0.0798083099,-0.0551252923,1.4536020604
O,0,1.1506504204,-0.0905177577,2.0648257243
H,0,-0.8842502077,-0.082714579,1.9983622938
C,0,1.2417708404,0.0541720949,-0.6461258446
H,0,1.2438986083,0.2157383087,-1.7229610418
H,0,2.0476324271,0.5314952149,-0.0943885841
C,0,2.3465075853,-2.1567789164,0.6308991296
C,0,1.1989655015,-2.7180615626,1.3113194238
H,0,1.3636362927,-3.1101866487,2.334087801
O,0,0.0709859384,-2.7126688199,0.8121372496
C,0,2.1213183883,-1.7329999683,-0.6761108074
H,0,2.9778517831,-1.4437305995,-1.2830341852
H,0,1.3055247143,-2.2155378791,-1.2083721233
C,0,-1.2827577542,-0.2618014455,-0.7019368403
H,0,-1.3490531226,-1.2921393433,-1.0754123936
H,0,-2.1293039897,-0.114333216,-0.0222154523
H,0,-1.4028646821,0.416151627,-1.554474633
C,0,3.6378149526,-1.9462884085,1.3563618203
H,0,3.7529630254,-0.890300652,1.634041542

H,0,3.6634061027,-2.5247948406,2.2864607257
H,0,4.5029550135,-2.2330657052,0.7479555515

B3PW91/6-31G**

E(RB3PW91) = -462.274895266

Zero-point correction= 0.182086 (Hartree/Particle)
Thermal correction to Energy= 0.193389
Thermal correction to Enthalpy= 0.194334
Thermal correction to Gibbs Free Energy= 0.146054
Sum of electronic and ZPE= -462.092810
Sum of electronic and thermal Energies= -462.081506
Sum of electronic and thermal Enthalpies= -462.080562
Sum of electronic and thermal Free Energies= -462.128841

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	121.354	40.376	101.612

C,0,0.0172940623,-0.0483776485,0.0071447662
C,0,0.0827689034,-0.0558189108,1.4525200464
O,0,1.156288078,-0.0922750463,2.0598730342
H,0,-0.8805173747,-0.0827047713,1.9981160651
C,0,1.2425718191,0.0523055859,-0.6473934937
H,0,1.2431015109,0.2160582737,-1.7230736422
H,0,2.045474284,0.5295720819,-0.0921906771
C,0,2.3462236809,-2.1552700405,0.6306898341
C,0,1.1978476295,-2.7164004328,1.308788024
H,0,1.3615519432,-3.1093309286,2.3311014993
O,0,0.0709828143,-2.7079531487,0.806041118
C,0,2.1214183254,-1.7306604381,-0.6766097744
H,0,2.9784894138,-1.4441342917,-1.282608885
H,0,1.3047623341,-2.2151481517,-1.2048431424
C,0,-1.2822500105,-0.2631455598,-0.7003856516
H,0,-1.3511461728,-1.2962811689,-1.0626096048
H,0,-2.1270782156,-0.1062521724,-0.0224527162
H,0,-1.3986759234,0.4064726444,-1.5584863485
C,0,3.6360419022,-1.9456086369,1.357291786
H,0,3.7435842096,-0.8921820702,1.6437340679
H,0,3.6638884505,-2.5314539989,2.2813876023
H,0,4.5014898197,-2.2219567289,0.7466265973

B3PW91/6-31+G*

E(RB3PW91) = -462.273579580

Zero-point correction= 0.182188 (Hartree/Particle)
Thermal correction to Energy= 0.193628
Thermal correction to Enthalpy= 0.194572
Thermal correction to Gibbs Free Energy= 0.145664
Sum of electronic and ZPE= -462.091391
Sum of electronic and thermal Energies= -462.079951
Sum of electronic and thermal Enthalpies= -462.079007
Sum of electronic and thermal Free Energies= -462.127916

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	121.504	40.402	102.937

C,0,0.013577885,-0.0442701712,0.0097776051
C,0,0.0600597541,-0.055518619,1.4568451391
O,0,1.1262193074,-0.0848837624,2.0805660913
H,0,-0.9057865194,-0.0907060948,1.9949352112
C,0,1.2450775291,0.0522147344,-0.6369105741
H,0,1.2501001119,0.2153850313,-1.7138808941
H,0,2.0512390049,0.5278358474,-0.0830640625
C,0,2.3473143811,-2.1607560108,0.6332053233
C,0,1.2084366695,-2.7230643249,1.3282293933
H,0,1.3777472651,-3.1060937687,2.352075317
O,0,0.0749757105,-2.729035435,0.8364805437
C,0,2.1118442252,-1.7342808081,-0.6732322063
H,0,2.9670458258,-1.4457948665,-1.2830854067
H,0,1.293903391,-2.2160866121,-1.203980438
C,0,-1.2796955295,-0.2537608082,-0.7129911476
H,0,-1.3383220319,-1.2776035873,-1.1073707371
H,0,-2.1333019138,-0.1238738406,-0.0384208348
H,0,-1.3957405487,0.4394430215,-1.5541972942
C,0,3.6460635299,-1.948390368,1.3452366455
H,0,3.7738792434,-0.888220153,1.6039423131
H,0,3.6762971439,-2.5105849311,2.2852274924
H,0,4.5031770576,-2.2525000272,0.7332730085

B3PW91/6-31+G**
E(RB3PW91) = -462.289517741

Zero-point correction= 0.181525 (Hartree/Particle)
Thermal correction to Energy= 0.192949

Thermal correction to Enthalpy= 0.193893
Thermal correction to Gibbs Free Energy= 0.145105
Sum of electronic and ZPE= -462.10799
Sum of electronic and thermal Energies= -462.096569
Sum of electronic and thermal Enthalpies= -462.095625
Sum of electronic and thermal Free Energies= -462.144413

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	121.077	40.529	102.683

C,0,0.0143312959,-0.0452923096,0.0091519727
C,0,0.0627373377,-0.055741607,1.4557454263
O,0,1.1316115661,-0.0877422285,2.0757629098
H,0,-0.9024083569,-0.0884264073,1.994436972
C,0,1.2463909044,0.0500728833,-0.6379836734
H,0,1.2495622519,0.216096976,-1.7136186308
H,0,2.0490706113,0.5257547307,-0.0801783709
C,0,2.3471247646,-2.1594378551,0.6327254047
C,0,1.207601338,-2.7218740721,1.3257166129
H,0,1.3765375347,-3.1072349322,2.3483214527
O,0,0.074781831,-2.7234475869,0.8310901635
C,0,2.1114264286,-1.7316687381,-0.6739152575
H,0,2.9673187561,-1.4466459113,-1.2828281662
H,0,1.2925881185,-2.2158345762,-1.2000349685
C,0,-1.2791351975,-0.2546510834,-0.7117599026
H,0,-1.3458250837,-1.2853640662,-1.0836363192
H,0,-2.1309978054,-0.1030772821,-0.0413524973
H,0,-1.3856550721,0.4221217516,-1.5658038752
C,0,3.6445965255,-1.9479761364,1.3457833048
H,0,3.7586834116,-0.892377605,1.6247183979
H,0,3.6814027345,-2.5274910656,2.2736293905
H,0,4.502367592,-2.230308436,0.7266901526

B3LYP/6-31G*
E(RB3LYP) = -462.437243006

Zero-point correction= 0.182642 (Hartree/Particle)
Thermal correction to Energy= 0.193842
Thermal correction to Enthalpy= 0.194787
Thermal correction to Gibbs Free Energy= 0.146698
Sum of electronic and ZPE= -462.254601
Sum of electronic and thermal Energies= -462.243401

Sum of electronic and thermal Enthalpies= -462.242456
Sum of electronic and thermal Free Energies= -462.290545

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	121.638	40.013	101.211

C,0,0.0162848408,-0.0546518171,0.0129153388
C,0,0.0824937719,-0.0498217997,1.4562564334
O,0,1.1605131779,-0.0912141573,2.0634787975
H,0,-0.8778899967,-0.0689505295,2.0060342256
C,0,1.2492103426,0.0254876221,-0.6534364354
H,0,1.2296552302,0.1980820408,-1.728415337
H,0,2.0415635529,0.5439076501,-0.1199303285
C,0,2.3411327294,-2.152198736,0.6368811611
C,0,1.1963835546,-2.7233107051,1.3084620668
H,0,1.356707025,-3.1242494784,2.327531739
O,0,0.065863929,-2.7094833151,0.8041879887
C,0,2.1165012225,-1.7029386514,-0.6739423863
H,0,2.9870888324,-1.4287028785,-1.2677629223
H,0,1.3313299019,-2.2175878655,-1.2215315435
C,0,-1.2875074846,-0.2628548401,-0.6978086111
H,0,-1.3427840705,-1.281133118,-1.1055928402
H,0,-2.1322325887,-0.1472813596,-0.0099874138
H,0,-1.4194833089,0.4400378029,-1.5288624901
C,0,3.6373319922,-1.947982411,1.3624944348
H,0,3.7745132041,-0.8867005348,1.6096709384
H,0,3.6490696047,-2.5009116465,2.3080880152
H,0,4.4983660274,-2.268086828,0.7639296613

B3LYP/6-31+G**
E(RB3LYP) = -462.473299317

Zero-point correction= 0.181419 (Hartree/Particle)
Thermal correction to Energy= 0.192684
Thermal correction to Enthalpy= 0.193628
Thermal correction to Gibbs Free Energy= 0.145332
Sum of electronic and ZPE= -462.291880
Sum of electronic and thermal Energies= -462.280615
Sum of electronic and thermal Enthalpies= -462.279671
Sum of electronic and thermal Free Energies= -462.327967

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K

Total 120.911 40.260 101.648

C,0,0.0131102333,-0.0546297406,0.0147696286
C,0,0.0647644799,-0.0502988853,1.458952848
O,0,1.141574101,-0.0875976063,2.0751112766
H,0,-0.8960052101,-0.0751262057,2.0033261401
C,0,1.2521001696,0.0204498025,-0.6474216863
H,0,1.2304464779,0.1956294231,-1.7214883776
H,0,2.0414514958,0.5415742425,-0.1120505805
C,0,2.3416518715,-2.1536150508,0.6402340038
C,0,1.205025593,-2.7276048349,1.3235849527
H,0,1.3685547569,-3.1213645109,2.3425298013
O,0,0.069238981,-2.7212716764,0.8230751856
C,0,2.1091005609,-1.7002692221,-0.6711117877
H,0,2.9807986337,-1.4291374565,-1.2639069252
H,0,1.3248849608,-2.2186971757,-1.216553598
C,0,-1.2855820224,-0.2549383859,-0.7069772529
H,0,-1.3341748063,-1.2662916446,-1.1323097297
H,0,-2.1348658127,-0.1542027165,-0.0240718642
H,0,-1.4117136223,0.461434999,-1.5264018435
C,0,3.6448037469,-1.9509649053,1.3532359655
H,0,3.7927710467,-0.8874355733,1.5837038082
H,0,3.6600417298,-2.4896119929,2.3058206181
H,0,4.4961341221,-2.2865764408,0.7506099154

BP86/6-31G*

E(RB-P86) = -462.436013768
Zero-point correction= 0.176546 (Hartree/Particle)
Thermal correction to Energy= 0.188234
Thermal correction to Enthalpy= 0.189178
Thermal correction to Gibbs Free Energy= 0.140031
Sum of electronic and ZPE= -462.259468
Sum of electronic and thermal Energies= -462.247780
Sum of electronic and thermal Enthalpies= -462.246836
Sum of electronic and thermal Free Energies= -462.295983

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	118.118	41.623	103.439

C,0,0.0033763553,-0.0180813358,-0.0010202267
C,0,0.0563222336,-0.0286453503,1.4586125919
O,0,1.1267554254,-0.0641108967,2.09335198
H,0,-0.9274180087,-0.048776669,1.9930784577

C,0,1.2304238663,0.101428425,-0.6555125155
H,0,1.2476558479,0.250482692,-1.7421012854
H,0,2.055247013,0.5455118424,-0.087899853
C,0,2.3671714931,-2.181875233,0.6250694127
C,0,1.2148715299,-2.7485213693,1.3211726957
H,0,1.4009504741,-3.1471979713,2.3508500673
O,0,0.0691165685,-2.7526031268,0.8341326342
C,0,2.1451129725,-1.7737207454,-0.6911327987
H,0,2.9973453583,-1.4662672633,-1.3094867326
H,0,1.2987889347,-2.229093094,-1.2165841157
C,0,-1.3034635471,-0.2488786924,-0.7111570813
H,0,-1.3903004308,-1.3067099831,-1.0243998431
H,0,-2.1568720101,-0.0436347345,-0.0399022947
H,0,-1.4068815531,0.383674099,-1.6102628663
C,0,3.6601452069,-1.9583582466,1.3623966363
H,0,3.7360446934,-0.9062695795,1.6970866663
H,0,3.708250246,-2.5864225836,2.2702706195
H,0,4.5414688251,-2.1824757377,0.7360983362

BP86/6-31+G**

E(RB-P86) = -462.470158606

Zero-point correction= 0.175362 (Hartree/Particle)
Thermal correction to Energy= 0.187172
Thermal correction to Enthalpy= 0.188117
Thermal correction to Gibbs Free Energy= 0.138493
Sum of electronic and ZPE= -462.294797
Sum of electronic and thermal Energies= -462.282986
Sum of electronic and thermal Enthalpies= -462.282042
Sum of electronic and thermal Free Energies= -462.331666

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	117.452	41.926	104.442

C,0,0.0006620828,-0.0193284536,0.000911032
C,0,0.041174667,-0.0316109684,1.4604450716
O,0,1.1115165293,-0.0619281329,2.1019498153
H,0,-0.940927607,-0.0608171242,1.9917094505
C,0,1.2334236106,0.0943534388,-0.6512543368
H,0,1.2462112364,0.2455716903,-1.7369765441
H,0,2.0550484761,0.5439692908,-0.083563467
C,0,2.3670908787,-2.182095556,0.6286186798
C,0,1.2220915083,-2.7497180903,1.3348855152

H,0,1.407763181,-3.138673684,2.3653510859
O,0,0.0722666647,-2.7611330521,0.849239866
C,0,2.1385728554,-1.7685046135,-0.6884486195
H,0,2.9932938969,-1.4642419462,-1.3038341611
H,0,1.2952725718,-2.2295010312,-1.2136359119
C,0,-1.3020889315,-0.2418141785,-0.7187836534
H,0,-1.3842233508,-1.2942362058,-1.0500331596
H,0,-2.1586094431,-0.0505393574,-0.0495860899
H,0,-1.399864823,0.4053250681,-1.6068264524
C,0,3.666596968,-1.9613135621,1.3546763761
H,0,3.754530366,-0.9058468111,1.6745545978
H,0,3.7153096107,-2.5767237081,2.2695185776
H,0,4.5390005446,-2.2017385669,0.7237428149

BB1K/6-31+G**

E(RB+HF-B95) = -462.218795429

Zero-point correction= 0.186368 (Hartree/Particle)
Thermal correction to Energy= 0.197353
Thermal correction to Enthalpy= 0.198297
Thermal correction to Gibbs Free Energy= 0.150778
Sum of electronic and ZPE= -462.032428
Sum of electronic and thermal Energies= -462.021442
Sum of electronic and thermal Enthalpies= -462.020498
Sum of electronic and thermal Free Energies= -462.068017

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	123.841	39.415	100.013

C,0,0.0414187642,-0.0758414176,0.01873396
C,0,0.1282720213,-0.0869193992,1.449514147
O,0,1.2146550135,-0.1371383975,2.0180358061
H,0,-0.8072230923,-0.1224123975,2.02089802
C,0,1.2605195288,0.0188229868,-0.641470118
H,0,1.2427467207,0.1894837571,-1.7097124046
H,0,2.0535202713,0.5141554674,-0.0984638517
C,0,2.317013729,-2.1304762554,0.6290723655
C,0,1.1660407915,-2.6781087837,1.2849367302
H,0,1.2912933316,-3.0680294393,2.3023668626
O,0,0.0582531689,-2.6391281754,0.7583876577
C,0,2.0990778374,-1.6994842445,-0.6739193006
H,0,2.9630234563,-1.4258663764,-1.2649470359
H,0,1.3015017725,-2.1972189743,-1.2079537643

C,0,-1.2514636925,-0.2919416774,-0.6790189608
H,0,-1.283550076,-1.3014527201,-1.0919053648
H,0,-2.086468932,-0.2043926171,0.0118745206
H,0,-1.398895512,0.4153404379,-1.4924610816
C,0,3.5950107442,-1.9221915193,1.3560143201
H,0,3.723764278,-0.8619258915,1.5793449945
H,0,3.5927250278,-2.4493558462,2.3069743291
H,0,4.4528763424,-2.25646407,0.7763586522

M06/6-31G*

E(RM06) = -462.124626271

Zero-point correction= 0.181253 (Hartree/Particle)
Thermal correction to Energy= 0.192648
Thermal correction to Enthalpy= 0.193592
Thermal correction to Gibbs Free Energy= 0.145020
Sum of electronic and ZPE= -461.943374
Sum of electronic and thermal Energies= -461.931978
Sum of electronic and thermal Enthalpies= -461.931034
Sum of electronic and thermal Free Energies= -461.979606

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	120.889	40.482	102.229

C,0,0.0414643659,-0.0376333999,0.0197657149
C,0,0.1014520877,-0.0669412584,1.463243307
O,0,1.1652966838,-0.1248358006,2.0756553938
H,0,-0.8733725931,-0.100001563,1.9978206307
C,0,1.2605731302,0.0606831289,-0.6336919734
H,0,1.2589668117,0.2252228093,-1.712934953
H,0,2.0813103461,0.5233305796,-0.0849545512
C,0,2.324030766,-2.1649760714,0.614191401
C,0,1.1759681328,-2.7069562924,1.3043324493
H,0,1.3538769803,-3.0923125059,2.3324365723
O,0,0.0467286575,-2.6833969917,0.8201539351
C,0,2.1016721571,-1.7399541093,-0.6868897841
H,0,2.962935007,-1.453135594,-1.2933572098
H,0,1.2761007079,-2.2051397491,-1.2261477024
C,0,-1.2454289361,-0.2784304606,-0.6893634652
H,0,-1.2646003422,-1.2979126541,-1.1035039313
H,0,-2.0960448978,-0.2032938231,0.0001972945
H,0,-1.4061932457,0.4247604144,-1.5166699851
C,0,3.6020259441,-1.9288509244,1.3407690149

H,0,3.7218243075,-0.8565350697,1.55758892
H,0,3.6077293769,-2.4476044957,2.3080069757
H,0,4.4777960445,-2.2566317235,0.7660124346

M06/6-31+G**

E(RM06) = -462.155872998

Zero-point correction= 0.180017 (Hartree/Particle)
Thermal correction to Energy= 0.191600
Thermal correction to Enthalpy= 0.192544
Thermal correction to Gibbs Free Energy= 0.143006
Sum of electronic and ZPE= -461.975856
Sum of electronic and thermal Energies= -461.964273
Sum of electronic and thermal Enthalpies= -461.963329
Sum of electronic and thermal Free Energies= -462.012867

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	120.231	40.757	104.261

C,0,0.0383694618,-0.0377167124,0.0212407144
C,0,0.0879033694,-0.0661630634,1.4652344446
O,0,1.1519469571,-0.1211289936,2.0830232542
H,0,-0.8853805022,-0.1029901812,1.9969116547
C,0,1.2617901889,0.0573909443,-0.6301919892
H,0,1.2568745175,0.2222148482,-1.7083294963
H,0,2.0801129735,0.5217071318,-0.0806104023
C,0,2.3247702037,-2.1661294843,0.6173352627
C,0,1.1828599138,-2.7112296777,1.3153949769
H,0,1.3612783671,-3.0917425183,2.3423785311
O,0,0.049981924,-2.6924048928,0.83258434
C,0,2.0975748536,-1.7381741823,-0.6847418631
H,0,2.9600662063,-1.4527324299,-1.2882343982
H,0,1.273170541,-2.2056834445,-1.2223981116
C,0,-1.2452585462,-0.2715960176,-0.6958937897
H,0,-1.2581803627,-1.2848565417,-1.1233154754
H,0,-2.0975991643,-0.2090242977,-0.0099101874
H,0,-1.4008682894,0.4422940685,-1.513044725
C,0,3.6083248629,-1.9322886904,1.3346135972
H,0,3.7357617877,-0.8589026037,1.5374812867
H,0,3.6152423679,-2.4387454239,2.3064299262
H,0,4.4753698654,-2.2726433896,0.7567029288

MP2/6-31G*

E(RHF) = -459.534397669

Zero-point correction= 0.185204 (Hartree/Particle)
Thermal correction to Energy= 0.196396
Thermal correction to Enthalpy= 0.197340
Thermal correction to Gibbs Free Energy= 0.149404
Sum of electronic and zero-point Energies= -460.770054
Sum of electronic and thermal Energies= -460.758862
Sum of electronic and thermal Enthalpies= -460.757918
Sum of electronic and thermal Free Energies= -460.805854

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	123.240	40.045	100.890

C,0,0.0274797265,-0.0366545534,0.0102300301
C,0,0.1151648647,-0.0717724109,1.456478621
O,0,1.2088885896,-0.1256046256,2.0495747581
H,0,-0.8330441794,-0.1051797868,2.0248242038
C,0,1.233687755,0.1035447313,-0.659226128
H,0,1.2273916079,0.2582479402,-1.7363374659
H,0,2.0584659332,0.5473875197,-0.1099243576
C,0,2.3400572294,-2.1648828688,0.6197232496
C,0,1.171801105,-2.6971131938,1.2923787656
H,0,1.3075565866,-3.09028034,2.3171827419
O,0,0.0399783423,-2.663284681,0.773991471
C,0,2.14640189,-1.7734466244,-0.6963468363
H,0,3.0068732955,-1.4796695515,-1.2941976122
H,0,1.3140793932,-2.2212505181,-1.2308548654
C,0,-1.2771727633,-0.2850955929,-0.6840027316
H,0,-1.3350337622,-1.3270910008,-1.0164286632
H,0,-2.1159321569,-0.1138423256,-0.0022115078
H,0,-1.4015727613,0.36724209,-1.5530211031
C,0,3.6158995819,-1.9315684422,1.3704501417
H,0,3.6920788693,-0.8799551121,1.6669555301
H,0,3.6400373308,-2.530534572,2.2860598944
H,0,4.4910249986,-2.1897416441,0.7673623829

MPW1k/6-31+G**
E(RmPW+HF-PW91) = -462.314623357

Zero-point correction= 0.186974 (Hartree/Particle)
Thermal correction to Energy= 0.198022
Thermal correction to Enthalpy= 0.198967

Thermal correction to Gibbs Free Energy= 0.151119
Sum of electronic and ZPE= -462.127649
Sum of electronic and thermal Energies= -462.116601
Sum of electronic and thermal Enthalpies= -462.115657
Sum of electronic and thermal Free Energies= -462.163505

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	124.261	39.357	100.704

C,0,0.0321711547,-0.0718089486,0.0155223274
C,0,0.1070001499,-0.0870133573,1.4493056519
O,0,1.1852707023,-0.1316600196,2.0313523492
H,0,-0.8355075038,-0.1248989936,2.0093087994
C,0,1.2537200139,0.023749823,-0.6400053644
H,0,1.2395585839,0.1923713312,-1.7091144926
H,0,2.0471260937,0.5178465159,-0.0969103808
C,0,2.3259361363,-2.1346794701,0.6329216909
C,0,1.1791451208,-2.6823031512,1.3011610529
H,0,1.3168967215,-3.0669504997,2.3192133294
O,0,0.0670860011,-2.6553970006,0.7853707468
C,0,2.1031102481,-1.7058639343,-0.6699580076
H,0,2.9651006503,-1.4293372453,-1.2633664874
H,0,1.3049657973,-2.2024484843,-1.2037614649
C,0,-1.2606859491,-0.277669091,-0.6901941821
H,0,-1.3068041968,-1.2881094556,-1.0997349248
H,0,-2.0992869459,-0.1739750215,-0.0052021828
H,0,-1.393635046,0.427935065,-1.5081988138
C,0,3.6121165071,-1.9323249117,1.3517306831
H,0,3.7466687556,-0.8754527344,1.587860174
H,0,3.6198525877,-2.472260289,2.2959912787
H,0,4.4643058957,-2.2602956891,0.7593687331

MPWLYP/6-31+G**
E(RmPW-LYP) = -462.291916971

Zero-point correction= 0.175633 (Hartree/Particle)
Thermal correction to Energy= 0.187293
Thermal correction to Enthalpy= 0.188237
Thermal correction to Gibbs Free Energy= 0.138994
Sum of electronic and ZPE= -462.116284
Sum of electronic and thermal Energies= -462.104624
Sum of electronic and thermal Enthalpies= -462.103680
Sum of electronic and thermal Free Energies= -462.152923

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	117.528	41.565	103.641

C,0,-0.0009125287,-0.0268406083,0.0099606636
C,0,0.0310605578,-0.0205697021,1.4667609046
O,0,1.1043849297,-0.0548464662,2.1132239746
H,0,-0.9485795413,-0.0380490948,1.9960043382
C,0,1.2473501961,0.0497091234,-0.6486222014
H,0,1.2393915326,0.2201021297,-1.7300612321
H,0,2.0490922252,0.5512532211,-0.0996789745
C,0,2.3595793525,-2.1793540306,0.6373861603
C,0,1.2256825784,-2.7641842444,1.3413607847
H,0,1.4138061651,-3.1622864845,2.3642112075
O,0,0.0694307566,-2.773448107,0.8575111074
C,0,2.1189147698,-1.7268695925,-0.6798417901
H,0,2.9869311387,-1.4456937687,-1.2848998314
H,0,1.3127383361,-2.2307419513,-1.220089542
C,0,-1.3025395224,-0.2380188538,-0.7231607377
H,0,-1.3690153273,-1.2747318973,-1.1010617286
H,0,-2.1633525063,-0.0861023021,-0.0524729575
H,0,-1.4045550799,0.4426780064,-1.5842662808
C,0,3.6710020615,-1.9630325958,1.3512990306
H,0,3.7883420424,-0.8996135809,1.6294598722
H,0,3.7131185421,-2.5448014932,2.2860026641
H,0,4.5322408221,-2.2451032575,0.7236350402

O3LYP/6-31+G**

E(RO3LYP) = -462.302164468

Zero-point correction= 0.180605 (Hartree/Particle)
Thermal correction to Energy= 0.192241
Thermal correction to Enthalpy= 0.193185
Thermal correction to Gibbs Free Energy= 0.143466
Sum of electronic and ZPE= -462.121560
Sum of electronic and thermal Energies= -462.109924
Sum of electronic and thermal Enthalpies= -462.108980
Sum of electronic and thermal Free Energies= -462.158698

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	120.633	40.784	104.642

C,0,-0.0040545867,-0.0247939024,0.0132722215
C,0,-0.003131862,0.0049636396,1.4665804045
O,0,1.0370904824,-0.0027160728,2.1341508054
H,0,-0.9909616208,-0.0062316772,1.9666200391
C,0,1.2493509596,0.0295170185,-0.6144382132
H,0,1.2604162697,0.20598271,-1.688425316
H,0,2.0404850237,0.5240709612,-0.0572720057
C,0,2.3593777763,-2.1831562943,0.6406311731
C,0,1.2518949393,-2.7939074745,1.3571894743
H,0,1.4686641131,-3.1875535121,2.3691314321
O,0,0.1051056951,-2.8421801592,0.8985873361
C,0,2.0873748357,-1.7221868756,-0.6561020781
H,0,2.9393354257,-1.4455253019,-1.2744324146
H,0,1.2799322953,-2.2253034991,-1.1812888064
C,0,-1.2825706699,-0.2237640816,-0.741861432
H,0,-1.3533973474,-1.2507005339,-1.1232673616
H,0,-2.1523632209,-0.0633820947,-0.0980687021
H,0,-1.3587032916,0.4543673671,-1.5982858089
C,0,3.6760773726,-1.9641380599,1.3208903355
H,0,3.8007580253,-0.9089258577,1.5966933844
H,0,3.745999989,-2.5444876006,2.2455717839
H,0,4.5174308887,-2.2404942535,0.6767842369

PW91/6-31+G**

E(RPW91-PW91) = -462.296804940

Zero-point correction= 0.176177 (Hartree/Particle)
Thermal correction to Energy= 0.187961
Thermal correction to Enthalpy= 0.188905
Thermal correction to Gibbs Free Energy= 0.138749
Sum of electronic and ZPE= -462.120628
Sum of electronic and thermal Energies= -462.108844
Sum of electronic and thermal Enthalpies= -462.107900
Sum of electronic and thermal Free Energies= -462.158056

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	117.947	41.843	105.562

C,0,0.0050559116,-0.0188493216,0.0016834317
C,0,0.0491639839,-0.0346379015,1.4590488516
O,0,1.1190275602,-0.0706176493,2.0960597352
H,0,-0.9294688894,-0.0624265796,1.991688164
C,0,1.2319210865,0.1012444082,-0.6506144254

H,0,1.2456731792,0.2477940489,-1.7345882477
H,0,2.0566645097,0.5407402806,-0.0835713752
C,0,2.3645384384,-2.1815561325,0.6241822223
C,0,1.2188383037,-2.7453885056,1.328167908
H,0,1.4022520786,-3.1360482704,2.3557594199
O,0,0.0713500703,-2.7501443643,0.8434291364
C,0,2.1402505673,-1.7739975397,-0.6906426785
H,0,2.9916813317,-1.4652574371,-1.3041744404
H,0,1.2934349206,-2.2250704121,-1.2144114224
C,0,-1.2952564814,-0.2486303535,-0.7124305239
H,0,-1.3874106282,-1.3092359598,-1.0054934833
H,0,-2.1496752807,-0.0256298288,-0.0542680134
H,0,-1.3827767587,0.3671278379,-1.6202258793
C,0,3.6570675676,-1.9560089169,1.3536434464
H,0,3.7200154982,-0.9108480087,1.7042414639
H,0,3.7201218579,-2.5953462248,2.2481876715
H,0,4.5316426654,-2.157758724,0.716989527

G4

G4 -0.2281312253D+01 EUMP2

Zero-point correction= 0.181123 (Hartree/Particle)
Thermal correction to Energy= 0.192362
Thermal correction to Enthalpy= 0.193306
Thermal correction to Gibbs Free Energy= 0.145126
Sum of electronic and ZPE= -462.291586
Sum of electronic and thermal Energies= -462.280347
Sum of electronic and thermal Enthalpies= -462.279402
Sum of electronic and thermal Free Energies= -462.327583

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	120.709	40.228	101.405

C,0,0.002998706,-0.0095691471,0.0001505863
C,0,0.0092224207,-0.0038705594,1.4421476763
O,0,1.0578233149,-0.0047086813,2.0890234273
H,0,-0.9730910083,-0.0621889254,1.9484404374
C,0,1.2576636734,0.1250343277,-0.612265048
H,0,1.2768009184,0.2992921237,-1.6853004308
H,0,1.9982184497,0.6779472769,-0.0425389267
C,0,2.3749268318,-1.9939623803,0.7246221198
C,0,1.2255988269,-2.6176255575,1.3325005572
H,0,1.3553176639,-3.0202216257,2.3551258521

O,0,0.1273687998,-2.6436170495,0.774622412
C,0,2.1964126794,-1.5467964554,-0.592773234
H,0,3.0812514732,-1.2323628988,-1.1407958556
H,0,1.4637538261,-2.0954408521,-1.176658745
C,0,-1.2585807819,-0.2617382697,-0.7646244716
H,0,-1.2474699436,-1.2682677111,-1.2011053699
H,0,-2.1315571027,-0.2066850965,-0.1074107649
H,0,-1.3935750186,0.45567843,-1.5812518143
C,0,3.6247639893,-1.7481411863,1.5104541503
H,0,3.7244336582,-0.6817235691,1.7482775396
H,0,3.6007742436,-2.2880961063,2.4617277919
H,0,4.5216301716,-2.0536883058,0.960852121

[3,3]-Sigmatropic rearrangent transition structures

B3PW91/6-31G*

E(RB3PW91) = -462.266382148

Zero-point correction= 0.185390 (Hartree/Particle)
Thermal correction to Energy= 0.195315
Thermal correction to Enthalpy= 0.196259
Thermal correction to Gibbs Free Energy= 0.151125
Sum of electronic and ZPE= -462.080992
Sum of electronic and thermal Energies= -462.071067
Sum of electronic and thermal Enthalpies= -462.070123
Sum of electronic and thermal Free Energies= -462.115258

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	122.562	37.851	94.993

C,0,-0.2673008117,0.2209630105,0.0145862565
C,0,0.1352113507,-0.0517330098,1.341757792
O,0,1.3009111667,0.2391407378,1.7021261845
H,0,-0.5278695431,-0.6446959109,1.9935322055
C,0,0.6961236622,1.0172679794,-0.7565276059
H,0,0.257304541,1.413633144,-1.6774883123
H,0,1.0554393531,1.8413799929,-0.1313991012
C,0,2.6576362291,-0.5527183915,-0.1174886038
C,0,1.9497553901,-1.724398793,0.2348599287
H,0,2.3499550141,-2.3753199027,1.0300220991
O,0,0.8050910333,-1.9167524141,-0.240237749
C,0,2.0294500845,0.2332785333,-1.1873192157
H,0,2.7112892894,0.9831459835,-1.600395538

H,0,1.7006220863,-0.446776638,-1.9800812935
C,0,-1.5736442528,-0.2138443162,-0.5499502202
H,0,-1.4121715087,-0.8674475117,-1.4169313063
H,0,-2.1627961305,-0.7717506604,0.1845529507
H,0,-2.1654979341,0.6454133891,-0.8936120806
C,0,3.955561282,-0.16479047,0.4984058135
H,0,3.8655931096,0.8149228368,0.9851599539
H,0,4.2721048669,-0.8875767985,1.2568424177
H,0,4.7473118617,-0.0825894964,-0.258651912

B3PW91/6-31G**

E(RB3PW91) = -462.282505168

Zero-point correction= 0.184663 (Hartree/Particle)
Thermal correction to Energy= 0.194610
Thermal correction to Enthalpy= 0.195554
Thermal correction to Gibbs Free Energy= 0.150383
Sum of electronic and ZPE= -462.097842
Sum of electronic and thermal Energies= -462.087895
Sum of electronic and thermal Enthalpies= -462.086951
Sum of electronic and thermal Free Energies= -462.132122

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	122.120	38.009	95.070

C,0,-0.2711050795,0.2138188113,-0.062108817
C,0,0.1060554592,-0.0412649304,1.2759976425
O,0,1.2546462783,0.2837189196,1.6616709882
H,0,-0.5578147701,-0.6485531312,1.9129971374
C,0,0.6885157869,1.0323912519,-0.8136195895
H,0,0.2613108672,1.4135423699,-1.7452906446
H,0,1.0098187031,1.8655049518,-0.180799478
C,0,2.6763976824,-0.4794311624,-0.1195989601
C,0,1.9923488627,-1.6684129292,0.2213281618
H,0,2.3921269926,-2.3035856906,1.0288048765
O,0,0.865149793,-1.8927211672,-0.2814066827
C,0,2.0529921888,0.2841953104,-1.207713499
H,0,2.7237864571,1.0491125549,-1.6086315007
H,0,1.7610219863,-0.4107460769,-2.0011756061
C,0,-1.550889848,-0.2582472626,-0.6548652165
H,0,-1.3498527705,-0.9117438626,-1.5122620671
H,0,-2.1421594748,-0.8265245497,0.0681791733
H,0,-2.1551369372,0.5825910616,-1.0183631063
C,0,3.9464810848,-0.0529593972,0.5262575313

H,0,3.8141454014,0.9229420692,1.0086316961
H,0,4.2654145391,-0.7647853128,1.2923625453
H,0,4.7520816678,0.0527219389,-0.2113715101

B3PW91/6-31+G*

E(RB3PW91) = -462.280936792

Zero-point correction= 0.184816 (Hartree/Particle)
Thermal correction to Energy= 0.194811
Thermal correction to Enthalpy= 0.195755
Thermal correction to Gibbs Free Energy= 0.150439
Sum of electronic and ZPE= -462.096121
Sum of electronic and thermal Energies= -462.086126
Sum of electronic and thermal Enthalpies= -462.085181
Sum of electronic and thermal Free Energies= -462.130498

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	122.246	38.029	95.377

C,0,-0.2747614715,0.2146723392,-0.0314882195
C,0,0.107090919,-0.0513215161,1.3048580405
O,0,1.2608807397,0.2626883046,1.6887437624
H,0,-0.5549345444,-0.6535666264,1.9472431217
C,0,0.6866450557,1.0224665284,-0.7929986496
H,0,0.2547437429,1.3996933705,-1.7254167919
H,0,1.0174798836,1.8618491369,-0.1713806471
C,0,2.6743050446,-0.5078164948,-0.118339761
C,0,1.9861512284,-1.6928407072,0.2340979833
H,0,2.3861342796,-2.3326519107,1.036773847
O,0,0.8515154676,-1.9141361616,-0.2569347484
C,0,2.0464277042,0.2663787034,-1.1968070396
H,0,2.7192532801,1.0329298894,-1.5942463701
H,0,1.7485130941,-0.4175397617,-1.9992497856
C,0,-1.5661776469,-0.2401545199,-0.6141947876
H,0,-1.3837863856,-0.8877989275,-1.4824306929
H,0,-2.1568675929,-0.8098859156,0.1101932762
H,0,-2.1657457788,0.6121361535,-0.9630088104
C,0,3.9572897528,-0.0943942093,0.5118840614
H,0,3.8455800269,0.8874215042,0.9915896089
H,0,4.2779102935,-0.8069659441,1.2784983585
H,0,4.7556453272,-0.0024438882,-0.237593331

B3PW91/6-31+G**
E(RB3PW91) = -462.296661130

Zero-point correction= 0.184082 (HartreeParticle)
Thermal correction to Energy= 0.194096
Thermal correction to Enthalpy= 0.195040
Thermal correction to Gibbs Free Energy= 0.149699
Sum of electronic and ZPE= -462.112579
Sum of electronic and thermal Energies= -462.102566
Sum of electronic and thermal Enthalpies= -462.101621
Sum of electronic and thermal Free Energies= -462.146962

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	121.797	38.194	95.427

C,0,-0.2749308054,0.2133630935,-0.0151236986
C,0,0.1119810137,-0.0547597988,1.3193221535
O,0,1.2698189069,0.2540759757,1.6963813357
H,0,-0.5509542088,-0.6537606136,1.9629560766
C,0,0.6865401524,1.0166518998,-0.7804967267
H,0,0.2518312545,1.3970571169,-1.7090941685
H,0,1.0244694146,1.8505658401,-0.1565077194
C,0,2.6707769734,-0.5221011884,-0.1156425837
C,0,1.9796683462,-1.7049209665,0.2390553675
H,0,2.3826445944,-2.345547434,1.0389207314
O,0,0.8416197587,-1.9200559424,-0.2473154786
C,0,2.0410328134,0.2546224971,-1.1906242926
H,0,2.7154231052,1.016282709,-1.5919287224
H,0,1.7344808812,-0.430928367,-1.9874962875
C,0,-1.5704783487,-0.2357525628,-0.5914307762
H,0,-1.3923277645,-0.8954890557,-1.4501186736
H,0,-2.1646837092,-0.7906791989,0.1397963778
H,0,-2.1606107143,0.617164088,-0.9505472418
C,0,3.9579694394,-0.114870051,0.5085748723
H,0,3.8468574673,0.8600756339,0.9999475915
H,0,4.284029458,-0.8354014308,1.2637092446
H,0,4.7486781544,-0.0131089144,-0.2458308164

B3LYP/6-31G*
E(RB3LYP) = -462.441598118

Zero-point correction= 0.184849 (Hartree/Particle)
Thermal correction to Energy= 0.194843

Thermal correction to Enthalpy= 0.195787
Thermal correction to Gibbs Free Energy= 0.150468
Sum of electronic and ZPE= -462.256749
Sum of electronic and thermal Energies= -462.246755
Sum of electronic and thermal Enthalpies= -462.245811
Sum of electronic and thermal Free Energies= -462.291131

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	122.266	38.008	95.382

C,0,-0.2795009542,0.2393866264,-0.0297980124
C,0,0.0929375703,-0.040196328,1.3088335134
O,0,1.2409986823,0.2653667896,1.7124018128
H,0,-0.5871921971,-0.639212066,1.9372080655
C,0,0.6919573158,1.0434124535,-0.7812167732
H,0,0.2693850767,1.4429036674,-1.707783396
H,0,1.0539502,1.8606817265,-0.1507608052
C,0,2.682061865,-0.5165918091,-0.1378905247
C,0,1.9980201271,-1.7030132404,0.2275697205
H,0,2.4166666451,-2.3339707866,1.0293812728
O,0,0.8644000864,-1.9416373461,-0.2541704049
C,0,2.045103262,0.2514860769,-1.2145241967
H,0,2.7139442766,1.0089451033,-1.6335579036
H,0,1.7116015918,-0.4313793696,-2.0012440021
C,0,-1.560863536,-0.2313341488,-0.6330272857
H,0,-1.3575265714,-0.9002595493,-1.4798321123
H,0,-2.1652838656,-0.7858730702,0.0918054465
H,0,-2.1567715631,0.6085056922,-1.0156384793
C,0,3.9562807923,-0.0810688598,0.5056270608
H,0,3.8168427656,0.8872951508,1.0043093821
H,0,4.290012871,-0.7996799384,1.2609046826
H,0,4.7574797728,0.0450736232,-0.2353108185

B3LYP/6-31+G**
E(RB3LYP) = -462.476965574

Zero-point correction= 0.183425 (Hartree/Particle)
Thermal correction to Energy= 0.193526
Thermal correction to Enthalpy= 0.194470
Thermal correction to Gibbs Free Energy= 0.148894
Sum of electronic and ZPE= -462.293540
Sum of electronic and thermal Energies= -462.283439
Sum of electronic and thermal Enthalpies= -462.282495

Sum of electronic and thermal Free Energies= -462.328072

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	121.439	38.384	95.924

C,0,-0.2858980901,0.2410289233,-0.0405253676
C,0,0.0771617782,-0.0428655991,1.3018043924
O,0,1.222778104,0.2682752423,1.7159481929
H,0,-0.6028859104,-0.6447164809,1.9241962698
C,0,0.6863339353,1.0440177364,-0.791034078
H,0,0.2656513942,1.4330173063,-1.721967078
H,0,1.0405182005,1.866834693,-0.1634604128
C,0,2.6902183083,-0.5061266693,-0.1397508764
C,0,2.0151004473,-1.6979848568,0.2327517419
H,0,2.4357846518,-2.3223058064,1.0360871618
O,0,0.8827925461,-1.9492926783,-0.251480394
C,0,2.0510039095,0.2604321689,-1.2154344096
H,0,2.7164440371,1.0243446844,-1.6260013858
H,0,1.7266057162,-0.4225477855,-2.0057693099
C,0,-1.5635755648,-0.2317139405,-0.6490366894
H,0,-1.3542042408,-0.9046467934,-1.4911252977
H,0,-2.1729727607,-0.781708964,0.0737252021
H,0,-2.1528345084,0.6080008776,-1.0397715105
C,0,3.9627677145,-0.0642464293,0.5019736424
H,0,3.8177639787,0.902742947,1.0016301823
H,0,4.3026639589,-0.7810966669,1.2548512512
H,0,4.7584612277,0.0682243402,-0.2425970689

BP86/6-31G*

E(RB-P86) = -462.445481788

Zero-point correction= 0.179298 (Hartree/Particle)
Thermal correction to Energy= 0.189510
Thermal correction to Enthalpy= 0.190454
Thermal correction to Gibbs Free Energy= 0.144774
Sum of electronic and ZPE= -462.266184
Sum of electronic and thermal Energies= -462.255972
Sum of electronic and thermal Enthalpies= -462.255028
Sum of electronic and thermal Free Energies= -462.300708

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	118.919	39.057	96.141

C,0,-0.2841851721,0.2275356975,-0.0231854781
C,0,0.0944231989,-0.0486673524,1.3222699411
O,0,1.257978649,0.2533136688,1.7219446383
H,0,-0.5925898232,-0.6481316564,1.9621302431
C,0,0.6942392495,1.0352199578,-0.7810991955
H,0,0.2621675695,1.4448175183,-1.7101468107
H,0,1.0540202148,1.8563999853,-0.1361900041
C,0,2.6838471352,-0.5214526374,-0.1260137481
C,0,1.9938502724,-1.7116444812,0.2438381771
H,0,2.4181594543,-2.3507691371,1.0514243038
O,0,0.8441874458,-1.9453175459,-0.234335247
C,0,2.0394988429,0.2474888024,-1.2111781865
H,0,2.7183596936,1.0024629575,-1.6433435025
H,0,1.7049331606,-0.4545471889,-1.9953112639
C,0,-1.57444743,-0.2378504349,-0.6201321928
H,0,-1.3818730803,-0.9192281884,-1.4709350451
H,0,-2.1863783913,-0.7860482578,0.1167759594
H,0,-2.1682822883,0.6117752238,-1.0099735062
C,0,3.9668010003,-0.0897190208,0.5107542141
H,0,3.836132397,0.8854277237,1.017926019
H,0,4.308076932,-0.8178261075,1.2666592748
H,0,4.7681195277,0.0387605309,-0.2428115168

BP86/6-31+G**
E(RB-P86) = -462.478811393

Zero-point correction= 0.178012 (Hartree/Particle)
Thermal correction to Energy= 0.188327
Thermal correction to Enthalpy= 0.189271
Thermal correction to Gibbs Free Energy= 0.143351
Sum of electronic and ZPE= -462.300799
Sum of electronic and thermal Energies= -462.290484
Sum of electronic and thermal Enthalpies= -462.289540
Sum of electronic and thermal Free Energies= -462.335460

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	118.177	39.449	96.646

C,0,-0.2882366428,0.232982327,-0.0219544422
C,0,0.0876109696,-0.0506774649,1.3240574402
O,0,1.2533862666,0.2504288523,1.72684253
H,0,-0.5971758211,-0.6507359407,1.961647761

C,0,0.6908525615,1.0352045755,-0.7845709259
H,0,0.2572009592,1.4346091076,-1.7160890662
H,0,1.0461249638,1.8623608853,-0.1451645454
C,0,2.6877674891,-0.5236422041,-0.1296844162
C,0,1.9999753319,-1.7156334849,0.2444026309
H,0,2.4229395576,-2.3534516751,1.0505473516
O,0,0.8482816835,-1.9522225858,-0.234415827
C,0,2.0433948083,0.2529553579,-1.2092525962
H,0,2.7227061026,1.0125821619,-1.6297410877
H,0,1.7158691298,-0.4441184618,-2.0004888102
C,0,-1.5831930978,-0.2222572613,-0.6155015447
H,0,-1.3964923787,-0.9020765078,-1.4683539263
H,0,-2.1965164305,-0.7673722759,0.1207331966
H,0,-2.168557523,0.6334468888,-1.0019286846
C,0,3.9763319301,-0.0995452781,0.4997318282
H,0,3.8522576717,0.8743907819,1.0100762369
H,0,4.3202538084,-0.8305594485,1.2498715592
H,0,4.7694087188,0.0290872576,-0.2609773431

BB1K/6-31+G**

E(RB+HF-B95) = -462.224689442

Zero-point correction= 0.188764 (Hartree/Particle)
Thermal correction to Energy= 0.198520
Thermal correction to Enthalpy= 0.199464
Thermal correction to Gibbs Free Energy= 0.154684
Sum of electronic and ZPE= -462.035925
Sum of electronic and thermal Energies= -462.026169
Sum of electronic and thermal Enthalpies= -462.025225
Sum of electronic and thermal Free Energies= -462.070005

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	124.573	37.257	94.248

C,0,-0.2522174915,0.2142368957,-0.0126938592
C,0,0.1486409436,-0.0498048528,1.3071718081
O,0,1.3064174559,0.2569206379,1.6492637248
H,0,-0.4915014291,-0.6504875703,1.9578644377
C,0,0.6981704969,1.0167141912,-0.7714899267
H,0,0.2633964382,1.402855717,-1.6892723371
H,0,1.0450378499,1.83565003,-0.1453764666
C,0,2.6484910215,-0.5227123224,-0.1191342561
C,0,1.9453382638,-1.6887847525,0.2248113754

H,0,2.3222883038,-2.3332366713,1.0226778941
O,0,0.8146117927,-1.8675264616,-0.2661731772
C,0,2.0305698573,0.2477637019,-1.1903550587
H,0,2.7054463621,0.9974506278,-1.5940482847
H,0,1.7125684978,-0.4345691797,-1.9753951964
C,0,-1.5388046284,-0.2404607361,-0.581049993
H,0,-1.351562964,-0.8914481735,-1.435627218
H,0,-2.1175748121,-0.8027321209,0.1464137356
H,0,-2.1354638572,0.6018812368,-0.9312681401
C,0,3.9235014567,-0.1225080763,0.5127402934
H,0,3.8036147006,0.8476698822,0.9959884778
H,0,4.2324581546,-0.8370154042,1.2706013905
H,0,4.7182428309,-0.0276013621,-0.2272407055

M06/6-31G*

E(RM06) = -462.129689365

Zero-point correction= 0.183939 (Hartree/Particle)
Thermal correction to Energy= 0.193876
Thermal correction to Enthalpy= 0.194820
Thermal correction to Gibbs Free Energy= 0.149757
Sum of electronic and ZPE= -461.945750
Sum of electronic and thermal Energies= -461.935813
Sum of electronic and thermal Enthalpies= -461.934869
Sum of electronic and thermal Free Energies= -461.979932

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	121.659	38.184	94.844

C,0,-0.2609346621,0.2764512788,0.0203595792
C,0,0.1067258831,-0.06532657,1.3455462811
O,0,1.2517137286,0.1952464823,1.7587362867
H,0,-0.6014118592,-0.6699746114,1.9457256505
C,0,0.7247603414,1.0581167538,-0.7028322683
H,0,0.3105594238,1.5232573991,-1.6053299026
H,0,1.1733403086,1.8148571994,-0.0478611657
C,0,2.6611299187,-0.5671342039,-0.1734419384
C,0,1.9722646093,-1.7343845376,0.2396955698
H,0,2.4208306782,-2.3496442595,1.044373
O,0,0.8320557454,-1.970767371,-0.2006484107
C,0,2.0023004461,0.1899514932,-1.2214738793
H,0,2.6702833662,0.9198092077,-1.6942674609
H,0,1.5713422562,-0.4839124833,-1.9718291576

C,0,-1.5092760621,-0.1983414603,-0.6187437087
H,0,-1.2631817691,-0.8585252665,-1.4654522404
H,0,-2.1234894601,-0.7778571754,0.0811343024
H,0,-2.1118899708,0.631600513,-1.0150875804
C,0,3.9087160218,-0.0961113525,0.4698373501
H,0,3.7289771909,0.8741037821,0.9594452655
H,0,4.2506043363,-0.7951353509,1.2427554346
H,0,4.7192417913,0.0501030132,-0.258671701

M06/6-31+G**

E(RM06) = -462.160559696

Zero-point correction= 0.182539 (Hartree/Particle)
Thermal correction to Energy= 0.192605
Thermal correction to Enthalpy= 0.193549
Thermal correction to Gibbs Free Energy= 0.148200
Sum of electronic and ZPE= -461.978021
Sum of electronic and thermal Energies= -461.967955
Sum of electronic and thermal Enthalpies= -461.967011
Sum of electronic and thermal Free Energies= -462.012360

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	120.861	38.608	95.446

C,0,-0.2690966542,0.2723461776,-0.0256654199
C,0,0.0796434728,-0.0586841971,1.309197469
O,0,1.2138998037,0.2256635083,1.7423140627
H,0,-0.6257226874,-0.6715778851,1.8996569948
C,0,0.7137766001,1.0639535494,-0.7418737681
H,0,0.3035930405,1.5086745233,-1.6548019903
H,0,1.1381944889,1.8348200863,-0.0885666234
C,0,2.6780202585,-0.5227691448,-0.1744975574
C,0,2.0095338756,-1.7017651599,0.2447878879
H,0,2.4586771697,-2.2986539792,1.0595220828
O,0,0.8788193589,-1.9680368225,-0.2089530831
C,0,2.018541813,0.2163583741,-1.2348712058
H,0,2.6791483376,0.9571642025,-1.697766628
H,0,1.6122726587,-0.46893765,-1.9875187484
C,0,-1.5019391927,-0.2225253197,-0.6787184274
H,0,-1.233989534,-0.8828314715,-1.5176728913
H,0,-2.1173850127,-0.8055137387,0.0146904594
H,0,-2.1056671951,0.5984875693,-1.0877435695
C,0,3.9110826322,-0.0255237046,0.4762869934

H,0,3.7085819765,0.9445911038,0.9553869489
H,0,4.2578085251,-0.7113416189,1.256605592
H,0,4.7216046211,0.1296446324,-0.2481690889

MP2/6-31G*

E(RHF) = -459.524961283

Zero-point correction= 0.188105 (Hartree/Particle)
Thermal correction to Energy= 0.197875
Thermal correction to Enthalpy= 0.198819
Thermal correction to Gibbs Free Energy= 0.153963
Sum of electronic and zero-point Energies= -460.780303
Sum of electronic and thermal Energies= -460.770532
Sum of electronic and thermal Enthalpies= -460.769588
Sum of electronic and thermal Free Energies= -460.814444

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	124.168	37.340	94.408

C,0,-0.0506955136,-0.0583164679,-0.0137158213
C,0,-0.0419600354,0.0137587589,1.3803063744
C,0,1.3073877248,0.0587077353,1.9591122884
C,0,2.1577188529,-1.2691412032,1.6867468858
C,0,2.089314527,-1.7452333881,0.2924985447
C,0,0.9338191914,-2.5301884199,0.0058360178
O,0,-0.0447225823,-2.4951778404,0.801789119
O,0,1.0809807559,-0.1931724196,-0.6172791142
H,0,3.1866548393,-1.0437692974,1.9843820159
H,0,0.842250414,-3.0076024745,-0.985731165
H,0,1.289944608,0.2324136103,3.0394372671
H,0,1.7400608118,-2.0283501288,2.3527054532
H,0,1.8780081705,0.8518497375,1.4666550164
C,0,-1.2743019744,-0.0441790395,2.216156049
H,0,-1.2770102377,-0.971708125,2.7996688819
H,0,-1.3183867665,0.7967284951,2.9164912234
H,0,-2.1734308043,-0.0340904579,1.5938074566
C,0,3.2805276558,-1.7035157459,-0.6045982764
H,0,3.6507393978,-0.6752752373,-0.6769229857
H,0,4.0919564736,-2.3312889471,-0.2171647699
H,0,3.0242412921,-2.0424173994,-1.6120077439
H,0,-0.987010801,-0.177106745,-0.5727807171

MPW1K/6-31+G**
E(RmPW+HF-PW91) = -462.321610385

Zero-point correction= 0.189543 (Hartree/Particle)
Thermal correction to Energy= 0.199249
Thermal correction to Enthalpy= 0.200193
Thermal correction to Gibbs Free Energy= 0.155486
Sum of electronic and ZPE= -462.132067
Sum of electronic and thermal Energies= -462.122361
Sum of electronic and thermal Enthalpies= -462.121417
Sum of electronic and thermal Free Energies= -462.166125

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	125.031	37.047	94.094

C,0,-0.2482152019,0.2110715373,0.0340533388
C,0,0.1782769297,-0.0446382214,1.3466871903
O,0,1.3525639042,0.2369210833,1.6560991642
H,0,-0.4564392621,-0.62794177,2.0181717624
C,0,0.6949801099,0.9986939557,-0.7602312931
H,0,0.2424175108,1.3621556294,-1.6795488231
H,0,1.0326016257,1.8408277889,-0.158998976
C,0,2.6344676589,-0.5678190445,-0.110204728
C,0,1.9086702612,-1.7228717117,0.2199829786
H,0,2.2783205388,-2.3892513167,1.003093759
O,0,0.7643204726,-1.8622344366,-0.254510188
C,0,2.0291085369,0.2380851987,-1.1707947076
H,0,2.7178191924,0.9895626245,-1.5489698646
H,0,1.7293049121,-0.4257335703,-1.9795704006
C,0,-1.5708893623,-0.197795331,-0.4893327243
H,0,-1.4399007738,-0.8436352865,-1.3581464134
H,0,-2.1409706072,-0.7479715502,0.2546498327
H,0,-2.1517717468,0.6690436303,-0.8068391009
C,0,3.9427071834,-0.2254877292,0.4912878006
H,0,3.8807630892,0.7480984015,0.9785648148
H,0,4.2410205204,-0.9561409161,1.2385152899
H,0,4.7206159492,-0.1644473622,-0.270799747

MPWLYP/6-31+G**
E(RmPW-LYP) = -462.296009798

Zero-point correction= 0.177747 (Hartree/Particle)
Thermal correction to Energy= 0.188156

Thermal correction to Enthalpy= 0.189100
Thermal correction to Gibbs Free Energy= 0.142920
Sum of electronic and ZPE= -462.118262
Sum of electronic and thermal Energies= -462.107854
Sum of electronic and thermal Enthalpies= -462.106909
Sum of electronic and thermal Free Energies= -462.153090

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	118.070	39.620	97.194

C,0,1.4998661204,0.1742048363,-0.4168267752
C,0,0.9542178399,-0.9917931588,-1.0414439541
O,0,-0.2307252769,-0.9764908562,-1.4971835156
H,0,1.5388530511,-1.9345827727,-1.0171183218
C,0,0.6608484419,1.3862502387,-0.4923626145
H,0,1.2225183687,2.2946029559,-0.2285263863
H,0,0.2350036583,1.4779570078,-1.5034876271
C,0,-1.4998718303,0.1748740168,0.4165779128
C,0,-0.9540679168,-0.9900524761,1.0430107776
H,0,-1.5385900551,-1.932948047,1.0202577237
O,0,0.2309416878,-0.9738860748,1.4985949531
C,0,-0.660905781,1.3870803995,0.4900497579
H,0,-1.2225995215,2.2949671346,0.2246637143
H,0,-0.2350507245,1.4805299252,1.5010097109
C,0,2.8267162709,0.1650225727,0.2844478955
H,0,2.6925317595,0.3701850657,1.3625014552
H,0,3.3266075218,-0.811383404,0.1904010689
H,0,3.4973052491,0.9468131182,-0.1153103177
C,0,-2.8267321095,0.1644413405,-0.2846625968
H,0,-2.6925902449,0.3679618227,-1.3630326486
H,0,-3.3264976498,-0.8118823894,-0.1891080074
H,0,-3.4974158591,0.9467627444,0.1138967954

O3LYP/6-31+G**
E(RO3LYP) = -462.306979054

Zero-point correction= 0.183042 (Hartree/Particle)
Thermal correction to Energy= 0.193261
Thermal correction to Enthalpy= 0.194205
Thermal correction to Gibbs Free Energy= 0.148311
Sum of electronic and ZPE= -462.123937
Sum of electronic and thermal Energies= -462.113719
Sum of electronic and thermal Enthalpies= -462.112774

Sum of electronic and thermal Free Energies= -462.158668

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	121.273	38.631	96.591

C,0,-0.2930409497,0.2392427024,-0.0161583501
C,0,0.061784808,-0.0546767424,1.3311114889
O,0,1.1991377471,0.2484724699,1.76239476
H,0,-0.6347709018,-0.6488337583,1.9458260393
C,0,0.6935597007,1.0280848936,-0.7608296208
H,0,0.2767540765,1.434991845,-1.6856886486
H,0,1.0616765383,1.8396428114,-0.1264849705
C,0,2.6937902032,-0.5326031796,-0.1357224733
C,0,2.0220637064,-1.726811672,0.250440114
H,0,2.4599637986,-2.3475942983,1.0497446892
O,0,0.8917297605,-1.9934920591,-0.2221530638
C,0,2.0368709941,0.2335801833,-1.1994678694
H,0,2.6999840927,0.9900164499,-1.6269693083
H,0,1.6956622542,-0.4510570864,-1.9813553661
C,0,-1.5762424523,-0.2077868299,-0.6286062923
H,0,-1.3842005442,-0.867805555,-1.4840019764
H,0,-2.1943308233,-0.7586432584,0.0849796756
H,0,-2.1535166326,0.6469361675,-1.0038625368
C,0,3.9743894537,-0.0900466473,0.4851222586
H,0,3.8463689943,0.8822506453,0.9775871624
H,0,4.3253788528,-0.8007278662,1.2377408873
H,0,4.7590817012,0.0327246448,-0.2723487165

PW91/6-31+G**

E(RPW91-PW91) = -462.306483841

Zero-point correction= 0.178974 (Hartree/Particle)
Thermal correction to Energy= 0.189217
Thermal correction to Enthalpy= 0.190161
Thermal correction to Gibbs Free Energy= 0.144417
Sum of electronic and ZPE= -462.127510
Sum of electronic and thermal Energies= -462.117267
Sum of electronic and thermal Enthalpies= -462.116322
Sum of electronic and thermal Free Energies= -462.162067

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	118.736	39.252	96.277

C,0,-0.2849259119,0.2245735515,-0.0270798516
C,0,0.088690826,-0.0549104251,1.3171743444
O,0,1.2526107887,0.2481918907,1.7177616208
H,0,-0.5925537478,-0.65532651,1.9538197351
C,0,0.6908324449,1.0294292074,-0.7859342959
H,0,0.2584697168,1.4247571463,-1.7170544298
H,0,1.0373582028,1.8579633144,-0.1470769233
C,0,2.6836099555,-0.5170870957,-0.1215602802
C,0,1.9988449216,-1.7097049139,0.2454013062
H,0,2.4179147864,-2.3472053553,1.0503880401
O,0,0.8507665795,-1.9445879755,-0.2373772484
C,0,2.043615587,0.2567063586,-1.2020144149
H,0,2.7218302298,1.0168313547,-1.6172494495
H,0,1.7251141111,-0.4405422301,-1.9939145959
C,0,-1.5716563142,-0.2374719759,-0.62327701
H,0,-1.3764032269,-0.9212574907,-1.4681746763
H,0,-2.1859694334,-0.7791960355,0.1110463081
H,0,-2.1562058532,0.6112000378,-1.0188721816
C,0,3.9632905143,-0.0895717073,0.5143021125
H,0,3.8281471211,0.87743931,1.0302159004
H,0,4.3087332501,-0.8214548844,1.2593634076
H,0,4.7566226175,0.0512420241,-0.24014998

G4

G4 -0.2301916524D+01 EUMP2

Zero-point correction= 0.183265 (Hartree/Particle)
Thermal correction to Energy= 0.193304
Thermal correction to Enthalpy= 0.194248
Thermal correction to Gibbs Free Energy= 0.148863
Sum of electronic and ZPE= -462.293199
Sum of electronic and thermal Energies= -462.283161
Sum of electronic and thermal Enthalpies= -462.282217
Sum of electronic and thermal Free Energies= -462.327601

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	121.300	38.283	95.520

C,0,0.0017022227,-0.0036469529,-0.0002532649
C,0,0.0049275064,-0.0013881309,1.4150272642
O,0,1.0889305173,0.0008497268,2.0332702219
H,0,-0.9530342303,-0.130045191,1.945567018

C,0,1.3187096835,0.1806457425,-0.6143953448
H,0,1.2516091294,0.4179996652,-1.6784557914
H,0,1.8594017587,0.9677216194,-0.0829033182
C,0,2.3957796296,-1.7070080685,0.8255132573
C,0,1.2499304446,-2.4377259252,1.2206980694
H,0,1.2476770412,-2.9211875185,2.2116468574
O,0,0.2199836705,-2.4055899185,0.5168281408
C,0,2.3081414092,-1.1076995318,-0.5081993878
H,0,3.2791278179,-0.7689254956,-0.8762769573
H,0,1.8697169071,-1.8296044661,-1.2017121453
C,0,-1.2389048191,-0.1609240413,-0.8098854979
H,0,-1.1758592837,-1.0650892234,-1.4279116427
H,0,-2.1229472354,-0.2522688695,-0.1730849672
H,0,-1.3831768812,0.6882028725,-1.4899236626
C,0,3.6067749376,-1.5686975802,1.6820844923
H,0,3.7816607617,-0.5129051698,1.9232549656
H,0,3.4945016509,-2.1125649274,2.6238876974
H,0,4.5039238793,-1.9378557423,1.1691241208

Methacrolein

B3PW91/6-31G*
E(RB3PW91) = -231.142672421

Zero-point correction= 0.090205 (Hartree/Particle)
Thermal correction to Energy= 0.095910
Thermal correction to Enthalpy= 0.096854
Thermal correction to Gibbs Free Energy= 0.061544
Sum of electronic and ZPE= -231.052467
Sum of electronic and thermal Energies= -231.046762
Sum of electronic and thermal Enthalpies= -231.045818
Sum of electronic and thermal Free Energies= -231.081128

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	60.185	19.141	74.317

C,0,-0.0111435293,-0.0020413587,-0.0243772156
C,0,-0.000508785,0.004616472,1.4559550784
O,0,0.9080428172,0.4483064552,2.127934234
H,0,-0.9050051977,-0.4359316068,1.9327196152
C,0,-1.0839846323,-0.525512781,-0.6345175843
H,0,-1.1730342888,-0.5699118968,-1.7169284679

H,0,-1.914961838,-0.9299935206,-0.0592917273
C,0,1.1821883225,0.5789941616,-0.7196113492
H,0,1.3267828106,1.6245080287,-0.4248120109
H,0,2.0943259046,0.0477192663,-0.4251864619
H,0,1.0783489615,0.5286346411,-1.8069128514

B3PW91/6-31G**
E(RB3PW91) = -231.150902108

Zero-point correction= 0.089863 (Hartree/Particle)
Thermal correction to Energy= 0.095588
Thermal correction to Enthalpy= 0.096532
Thermal correction to Gibbs Free Energy= 0.061161
Sum of electronic and ZPE= -231.061040
Sum of electronic and thermal Energies= -231.055314
Sum of electronic and thermal Enthalpies= -231.054370
Sum of electronic and thermal Free Energies= -231.089741

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	59.983	19.210	74.445

C,0,-0.0111471115,-0.0019548138,-0.0253577679
C,0,-0.0002514439,0.0046218023,1.4551784238
O,0,0.909182961,0.4482350638,2.1260935466
H,0,-0.9055644368,-0.4359840355,1.9303503772
C,0,-1.0842400408,-0.5252576306,-0.6347309454
H,0,-1.1731152499,-0.5694757831,-1.7163736641
H,0,-1.9132046611,-0.9285912152,-0.0571620261
C,0,1.1819200088,0.5786498803,-0.7197817747
H,0,1.3254770306,1.6229921583,-0.4242337386
H,0,2.0925368197,0.0482567202,-0.423017986
H,0,1.0794566692,0.5278957141,-1.8059931857

B3PW91/6-31+G*
E(RB3PW91) = -231.151878311

Zero-point correction= 0.090015 (Hartree/Particle)
Thermal correction to Energy= 0.095713
Thermal correction to Enthalpy= 0.096657
Thermal correction to Gibbs Free Energy= 0.061390
Sum of electronic and ZPE= -231.061863
Sum of electronic and thermal Energies= -231.056166
Sum of electronic and thermal Enthalpies= -231.055221

Sum of electronic and thermal Free Energies= -231.090488

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	60.061	19.175	74.226

C,0,-0.0073057877,-0.0002328195,-0.0228008191
C,0,-0.0033941697,0.001980109,1.4579162057
O,0,0.901494939,0.4436480694,2.1394782316
H,0,-0.9066432343,-0.4386205947,1.9338350002
C,0,-1.0824710878,-0.5248284731,-0.633311485
H,0,-1.1711671257,-0.5682652454,-1.7161793213
H,0,-1.9133905981,-0.9300577346,-0.0579512144
C,0,1.1836650086,0.5806993205,-0.7225329348
H,0,1.328800841,1.6275219757,-0.4317571246
H,0,2.0979026367,0.050274072,-0.4322151246
H,0,1.0735591232,0.5272691815,-1.8095101546

B3PW91/6-31+G**

E(RB3PW91) = -231.160028276

Zero-point correction= 0.089674 (Hartree/Particle)
Thermal correction to Energy= 0.095390
Thermal correction to Enthalpy= 0.096334
Thermal correction to Gibbs Free Energy= 0.061018
Sum of electronic and ZPE= -231.070354
Sum of electronic and thermal Energies= -231.064638
Sum of electronic and thermal Enthalpies= -231.063694
Sum of electronic and thermal Free Energies= -231.099010

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	59.858	19.247	74.330

C,0,-0.0073423627,-0.0002189918,-0.0237371507
C,0,-0.0032448344,0.0022356222,1.457208707
O,0,0.9025731875,0.4443106168,2.1374252168
H,0,-0.9070666757,-0.4384959349,1.9314960199
C,0,-1.0826670357,-0.5247997628,-0.6336558672
H,0,-1.1705444059,-0.5679318166,-1.7156899773
H,0,-1.9114892888,-0.9288357398,-0.0560392436
C,0,1.1834249062,0.580356011,-0.7227174512
H,0,1.3279840156,1.6256177324,-0.4301198672

H,0,2.0958616722,0.0499675652,-0.4307522542
H,0,1.0735613669,0.5271825591,-1.8084468734

B3LYP/6-31G*
E(RB3LYP) = -231.233543295

Zero-point correction= 0.090102 (Hartree/Particle)
Thermal correction to Energy= 0.095782
Thermal correction to Enthalpy= 0.096726
Thermal correction to Gibbs Free Energy= 0.061480
Sum of electronic and ZPE= -231.143442
Sum of electronic and thermal Energies= -231.137762
Sum of electronic and thermal Enthalpies= -231.136818
Sum of electronic and thermal Free Energies= -231.172063

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	60.104	19.103	74.180

C,0,-0.0136364048,-0.0032287967,-0.0228660986
C,0,-0.0011583322,0.0040675482,1.4600003368
O,0,0.9099731371,0.4487882283,2.1314475794
H,0,-0.904505583,-0.4358968484,1.9384539841
C,0,-1.0858129031,-0.5262586583,-0.6359963838
H,0,-1.1724138138,-0.569309465,-1.7182695638
H,0,-1.9182414895,-0.9315115983,-0.0644021573
C,0,1.1835553479,0.5797331946,-0.7207732651
H,0,1.3285755338,1.6256482059,-0.427291974
H,0,2.0963581004,0.0489001801,-0.4272978277
H,0,1.0783569525,0.5284558704,-1.808033371

B3LYP/6-31+G**
E(RB3LYP) = -231.254106891

Zero-point correction= 0.089521 (Hartree/Particle)
Thermal correction to Energy= 0.095212
Thermal correction to Enthalpy= 0.096157
Thermal correction to Gibbs Free Energy= 0.060905
Sum of electronic and ZPE= -231.164586
Sum of electronic and thermal Energies= -231.158894
Sum of electronic and thermal Enthalpies= -231.157950
Sum of electronic and thermal Free Energies= -231.193202

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 59.747 19.214 74.193

C,0,-0.0054420687,0.000745692,-0.0214737479
C,0,0.003735269,0.0219067477,1.4620480208
O,0,1.0155656468,0.018286659,2.1411592777
H,0,-0.9989348801,0.0419102073,1.9402962374
C,0,-1.2029808873,0.0067995777,-0.6321408502
H,0,-1.3001989394,-0.0077642075,-1.7137820091
H,0,-2.1255233752,0.0266800758,-0.0566497793
C,0,1.3217022224,-0.0260581269,-0.7268494018
H,0,1.9218760541,0.8474686149,-0.4505750246
H,0,1.9002638496,-0.9056286715,-0.4248759536
H,0,1.1943023595,-0.0403713451,-1.8121855103

BP86/6-31G*
E(RB-P86) = -231.227308741

Zero-point correction= 0.087237 (Hartree/Particle)
Thermal correction to Energy= 0.093057
Thermal correction to Enthalpy= 0.094001
Thermal correction to Gibbs Free Energy= 0.058444
Sum of electronic and ZPE= -231.140071
Sum of electronic and thermal Energies= -231.134252
Sum of electronic and thermal Enthalpies= -231.133308
Sum of electronic and thermal Free Energies= -231.168864

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 58.394 19.656 74.836

C,0,-0.0106243262,-0.0016550075,-0.0236693897
C,0,-0.0001307815,0.0046555688,1.4631972039
O,0,0.9179339365,0.4522235095,2.1444224102
H,0,-0.9168856724,-0.4413367984,1.9402139692
C,0,-1.0934954169,-0.529389465,-0.6387632878
H,0,-1.1851346974,-0.574858125,-1.7296351819
H,0,-1.9296885189,-0.9360278334,-0.0557045264
C,0,1.1887806497,0.5817173375,-0.7239297659
H,0,1.3360393921,1.6353854444,-0.4262106969
H,0,2.1087634908,0.0480457903,-0.4250102408
H,0,1.0854924895,0.5306274398,-1.8199392348

BP86/6-31+G**

E(RB-P86) = -231.246430061

Zero-point correction= 0.086741 (Hartree/Particle)
Thermal correction to Energy= 0.092566
Thermal correction to Enthalpy= 0.093510
Thermal correction to Gibbs Free Energy= 0.057978
Sum of electronic and ZPE= -231.159689
Sum of electronic and thermal Energies= -231.153864
Sum of electronic and thermal Enthalpies= -231.152920
Sum of electronic and thermal Free Energies= -231.188452

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	58.086	19.774	74.784

C,0,-0.0065676383,0.0002676178,-0.0229134684
C,0,-0.0034395235,0.0019918709,1.4646571545
O,0,0.9115136496,0.4480155387,2.1555712476
H,0,-0.9181808476,-0.4437470426,1.9398628883
C,0,-1.0920588067,-0.5287553919,-0.6379481093
H,0,-1.1822033385,-0.5728102225,-1.728283788
H,0,-1.9261182956,-0.9351099214,-0.0530958966
C,0,1.1901049341,0.583253125,-0.7274687872
H,0,1.3376890396,1.6364234956,-0.4317009711
H,0,2.1103455767,0.0500937541,-0.4319640248
H,0,1.0799657954,0.5297650371,-1.821744986

BB1K/6-31+G**

E(RB+HF-B95) = -231.125265725

Zero-point correction= 0.091833 (Hartree/Particle)
Thermal correction to Energy= 0.097489
Thermal correction to Enthalpy= 0.098434
Thermal correction to Gibbs Free Energy= 0.063261
Sum of electronic and ZPE= -231.033433
Sum of electronic and thermal Energies= -231.027776
Sum of electronic and thermal Enthalpies= -231.026832
Sum of electronic and thermal Free Energies= -231.062005

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	61.176	18.929	74.028

C,0,-0.0085715505,-0.0007978983,-0.0281780579
C,0,-0.0031956496,0.0033143725,1.4451113941
O,0,0.8980462598,0.4434564904,2.1112018252
H,0,-0.8980238789,-0.4325390498,1.9207453861
C,0,-1.0757598226,-0.5217239438,-0.6304099191
H,0,-1.1646845293,-0.5661405034,-1.705544553
H,0,-1.897216312,-0.9216504205,-0.0519296458
C,0,1.1778648873,0.5770169437,-0.7162129437
H,0,1.3179338747,1.6153229166,-0.4232045475
H,0,2.0820454659,0.048840262,-0.4211882287
H,0,1.0726118006,0.5242886916,-1.7954194507

M06/6-31G*

E(RM06) = -231.071524886

Zero-point correction= 0.089809 (Hartree/Particle)
Thermal correction to Energy= 0.095443
Thermal correction to Enthalpy= 0.096387
Thermal correction to Gibbs Free Energy= 0.061318
Sum of electronic and ZPE= -230.981715
Sum of electronic and thermal Energies= -230.976082
Sum of electronic and thermal Enthalpies= -230.975138
Sum of electronic and thermal Free Energies= -231.010207

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	59.891	19.133	73.809

C,0,-0.0072679561,0.0009557556,-0.0252813712
C,0,0.0152543818,0.0247674114,1.450565013
O,0,1.0219973032,-0.0733696241,2.1146520344
H,0,-0.9880017442,0.142852649,1.9285964203
C,0,-1.1936286348,0.1195886769,-0.6295638515
H,0,-1.298857015,0.1117250578,-1.7131475897
H,0,-2.110330819,0.2299858093,-0.0496054922
C,0,1.3048410774,-0.1545071141,-0.7182857832
H,0,1.9876050458,0.6582195324,-0.4389932194
H,0,1.7981565321,-1.0841129151,-0.4066570139
H,0,1.1887895359,-0.1620003221,-1.8073078876

M06/6-31+G**

E(RM06) = -231.089043889
Zero-point correction= 0.089226 (Hartree/Particle)

Thermal correction to Energy= 0.094903
Thermal correction to Enthalpy= 0.095847
Thermal correction to Gibbs Free Energy= 0.060676
Sum of electronic and ZPE= -230.999818
Sum of electronic and thermal Energies= -230.994141
Sum of electronic and thermal Enthalpies= -230.993196
Sum of electronic and thermal Free Energies= -231.028368

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	59.553	19.278	74.025

C,0,-0.0045900151,0.0006164211,-0.0248790688
C,0,0.0062584816,0.0188598858,1.4517235697
O,0,1.0114367571,0.1099562546,2.123202801
H,0,-0.99906824,-0.0589030547,1.9283285661
C,0,-1.1945935236,-0.1063848124,-0.630023534
H,0,-1.2939702606,-0.1276506466,-1.7129114773
H,0,-2.1130902434,-0.1762498142,-0.0486884873
C,0,1.3108365959,0.1026278646,-0.7206443034
H,0,1.8258479939,1.0275036445,-0.4361905034
H,0,1.9714799218,-0.7177230504,-0.4171950602
H,0,1.1915709216,0.0808502955,-1.8077512434

MP2/6-31G*
-0.6858933286D+00 EUMP2

Zero-point correction= 0.091312 (Hartree/Particle)
Thermal correction to Energy= 0.096986
Thermal correction to Enthalpy= 0.097930
Thermal correction to Gibbs Free Energy= 0.062710
Sum of electronic and ZPE= -230.394092
Sum of electronic and thermal Energies= -230.388417
Sum of electronic and thermal Enthalpies= -230.387473
Sum of electronic and thermal Free Energies= -230.422694

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	60.860	19.027	74.128

C,0,-0.0091664391,0.0012006131,-0.0233970411
C,0,0.0095264571,0.0249714687,1.4545389897
O,0,1.0360492061,-0.0753656082,2.1211776972

H,0,-0.9794159401,0.1414371888,1.9452603284
C,0,-1.1996420952,0.120323419,-0.6379537921
H,0,-1.2954962723,0.1118900058,-1.7194039044
H,0,-2.1179184958,0.2305467808,-0.0662571851
C,0,1.309949745,-0.154824247,-0.7175905507
H,0,1.9847722193,0.6595671589,-0.4395429985
H,0,1.7943828346,-1.085458465,-0.409095641
H,0,1.1855164875,-0.160183398,-1.8027646433

MPW1K/6-31+G**

E(RmPW+HF-PW91) = -231.173768197

Zero-point correction= 0.092286 (Hartree/Particle)
Thermal correction to Energy= 0.097914
Thermal correction to Enthalpy= 0.098858
Thermal correction to Gibbs Free Energy= 0.063720
Sum of electronic and ZPE= -231.081482
Sum of electronic and thermal Energies= -231.075855
Sum of electronic and thermal Enthalpies= -231.074910
Sum of electronic and thermal Free Energies= -231.110048

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	61.442	18.807	73.954

C,0,-0.0084755985,-0.0008833008,-0.0257560081
C,0,-0.0031121037,0.0031251041,1.448905191
O,0,0.8967506769,0.4430832542,2.116560523
H,0,-0.8977736711,-0.4331945358,1.9242227451
C,0,-1.0754213119,-0.521956335,-0.6305586333
H,0,-1.1614827951,-0.5647315559,-1.7062444924
H,0,-1.8991725449,-0.9234682864,-0.0562279828
C,0,1.1779226989,0.5775423014,-0.7175245841
H,0,1.3193597131,1.6163147087,-0.4253378059
H,0,2.0833393492,0.0485823277,-0.4261742137
H,0,1.0691161324,0.5249741786,-1.7968934798

MPWLYP/6-31+G**

E(RmPW-LYP) = -231.159523432

Zero-point correction= 0.086807 (Hartree/Particle)
Thermal correction to Energy= 0.092595
Thermal correction to Enthalpy= 0.093539
Thermal correction to Gibbs Free Energy= 0.058100

Sum of electronic and ZPE= -231.072717
Sum of electronic and thermal Energies= -231.066928
Sum of electronic and thermal Enthalpies= -231.065984
Sum of electronic and thermal Free Energies= -231.101424

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	58.104	19.705	74.589

C,0,-0.0091917784,-0.0010158253,-0.0201584696
C,0,-0.0047323563,0.0008273472,1.4703853216
O,0,0.9122884336,0.447671199,2.1622822618
H,0,-0.9156239104,-0.4432713707,1.9475792395
C,0,-1.0933205044,-0.5292846354,-0.6397192664
H,0,-1.1790156912,-0.5707963602,-1.728465234
H,0,-1.9289323652,-0.9366998787,-0.0622672695
C,0,1.1912330701,0.5841727002,-0.7292411791
H,0,1.3394389334,1.6365451776,-0.4362813759
H,0,2.1113398897,0.0517060856,-0.4373949524
H,0,1.0775668245,0.5295334215,-1.8217478169

O3LYP/6-31+G**

E(RO3LYP) = -231.170882797

Zero-point correction= 0.089299 (Hartree/Particle)
Thermal correction to Energy= 0.095025
Thermal correction to Enthalpy= 0.095970
Thermal correction to Gibbs Free Energy= 0.060634
Sum of electronic and ZPE= -231.081584
Sum of electronic and thermal Energies= -231.075857
Sum of electronic and thermal Enthalpies= -231.074913
Sum of electronic and thermal Free Energies= -231.110249

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	59.629	19.334	74.370

C,0,-0.0059281405,0.0004362929,-0.0201045265
C,0,-0.0027926615,0.0010007481,1.4656260142
O,0,0.9006129302,0.4413964039,2.1540993372
H,0,-0.9086145513,-0.4412895119,1.9360075494
C,0,-1.0831482805,-0.5246685019,-0.6346720803
H,0,-1.1689447339,-0.5657622758,-1.7169100743
H,0,-1.9143035488,-0.9305301933,-0.0624883351

C,0,1.1842708398,0.581621367,-0.7267606631
H,0,1.3308134259,1.6274899484,-0.4382542084
H,0,2.0988452899,0.0525729207,-0.4399902388
H,0,1.070239976,0.5271206628,-1.8115815152

PW91/6-31+G**

E(RPW91-PW91) = -231.157173318

Zero-point correction= 0.087169 (Hartree/Particle)
Thermal correction to Energy= 0.092982
Thermal correction to Enthalpy= 0.093926
Thermal correction to Gibbs Free Energy= 0.058422
Sum of electronic and ZPE= -231.070004
Sum of electronic and thermal Energies= -231.064192
Sum of electronic and thermal Enthalpies= -231.063247
Sum of electronic and thermal Free Energies= -231.098752

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	58.347	19.717	74.725

C,0,-0.0025160014,0.0006376371,-0.0229510452
C,0,0.0054733195,0.0224406879,1.4610354114
O,0,1.0244802969,0.0197192345,2.146417623
H,0,-1.0075616295,0.0422822815,1.939121287
C,0,-1.2090252564,0.0067724417,-0.6344966046
H,0,-1.3107558214,-0.0080359123,-1.7222607319
H,0,-2.1334624234,0.0270578767,-0.0491546974
C,0,1.3237708656,-0.0265088987,-0.7276342709
H,0,1.9282441437,0.850035095,-0.4456087503
H,0,1.9056783657,-0.9097851888,-0.4202860405
H,0,1.2000393913,-0.0406400311,-1.8192109215

G4

G4 -0.1103296399D+01 EUMP2

Zero-point correction= 0.089463 (Hartree/Particle)
Thermal correction to Energy= 0.095156
Thermal correction to Enthalpy= 0.096100
Thermal correction to Gibbs Free Energy= 0.060827
Sum of electronic and ZPE= -231.162584
Sum of electronic and thermal Energies= -231.156891
Sum of electronic and thermal Enthalpies= -231.155947
Sum of electronic and thermal Free Energies= -231.191221

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	59.711	19.172	74.240

C,0,0.0003422982,0.0000219855,-0.0009485166
C,0,0.001606399,-0.0000680774,1.4805434352
O,0,1.0024802314,-0.0001272487,2.1590031741
H,0,-1.010694623,0.000013281,1.9431363599
C,0,-1.1835412882,0.0001793986,-0.6222722821
H,0,-1.272751022,0.000284391,-1.7034960667
H,0,-2.1109303232,0.0002207511,-0.0565785217
C,0,1.3366985329,-0.0000782082,-0.6848573491
H,0,1.921960046,0.8747499903,-0.3836926133
H,0,1.9213463385,-0.8756522549,-0.3846447094
H,0,1.2306243468,0.000516472,-1.771839004

Methacrolein Dimer

B3PW91/6-31G*

E(RB3PW91) = -462.321872340

Zero-point correction= 0.187855 (Hartree/Particle)
Thermal correction to Energy= 0.198072
Thermal correction to Enthalpy= 0.199016
Thermal correction to Gibbs Free Energy= 0.152823
Sum of electronic and ZPE= -462.134017
Sum of electronic and thermal Energies= -462.123800
Sum of electronic and thermal Enthalpies= -462.122856
Sum of electronic and thermal Free Energies= -462.169049

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	124.292	38.437	97.222

C,0,-0.0449092878,0.1673561875,0.001964321
C,0,-0.1581696515,0.1172164548,1.3342507863
H,0,0.8886230792,0.3883232244,-0.5076034837
O,0,-1.040394738,-0.0554448388,-0.9068244165
C,0,-2.8729611712,1.3423049206,-0.1865312816
O,0,-2.2591027652,2.3474583227,-0.4390409671
H,0,-3.9098512632,1.3832423405,0.2272434866
C,0,1.0088079241,0.4113404876,2.2289157238
H,0,1.9107689693,0.6476832232,1.6543428142

H,0,1.2400535152,-0.4414872348,2.8829060755
H,0,0.8024159599,1.2672228656,2.887371035
C,0,-2.3634474398,-0.0847258552,-0.3962014533
C,0,-3.2249817739,-0.7434121344,-1.4728375962
H,0,-2.9199231003,-1.7868964483,-1.5994299358
H,0,-4.285144579,-0.721463225,-1.1989005886
H,0,-3.0956793616,-0.2253861436,-2.4280857601
C,0,-2.4285306426,-0.8451610772,0.9370884889
H,0,-2.1404377725,-1.8840950234,0.7356827779
H,0,-3.4618587069,-0.8612191904,1.3045252378
C,0,-1.4800592439,-0.226079314,1.9655985108
H,0,-1.9313662435,0.6721123307,2.417834159
H,0,-1.3303397068,-0.9291478723,2.797048066

B3PW91/6-31G**

E(RB3PW91) = -462.337721716

Zero-point correction= 0.187160 (Hartree/Particle)
Thermal correction to Energy= 0.197397
Thermal correction to Enthalpy= 0.198341
Thermal correction to Gibbs Free Energy= 0.152116
Sum of electronic and ZPE= -462.150562
Sum of electronic and thermal Energies= -462.140324
Sum of electronic and thermal Enthalpies= -462.139380
Sum of electronic and thermal Free Energies= -462.185605

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	123.869	38.583	97.289

C,0,-0.0431876999,0.1629414375,0.0036262607
C,0,-0.159330247,0.1135262223,1.3356922444
H,0,0.8926768946,0.3824643985,-0.5013824319
O,0,-1.0380514007,-0.0589924253,-0.9063936598
C,0,-2.8665176984,1.3452766077,-0.1878561344
O,0,-2.2479837791,2.347466781,-0.4406591396
H,0,-3.9033292502,1.3884043276,0.2260397069
C,0,1.0055285579,0.4069109849,2.2324018083
H,0,1.9081533641,0.6408427572,1.6601933321
H,0,1.2331678536,-0.444672069,2.8873808421
H,0,0.7986730455,1.2631204143,2.8883996419
C,0,-2.3619547169,-0.0838245525,-0.3975294477
C,0,-3.2244432531,-0.7388480449,-1.4752102996

H,0,-2.9241163238,-1.7826609646,-1.6007434928
H,0,-4.2838141314,-0.7119667405,-1.2028267331
H,0,-3.0912293048,-0.221673369,-2.4291125246
C,0,-2.4313527761,-0.8436916002,0.9355454009
H,0,-2.1467607489,-1.8827013349,0.7342060919
H,0,-3.464702643,-0.856326012,1.3003258813
C,0,-1.4825548907,-0.2274364676,1.9648020379
H,0,-1.9310410823,0.6713892916,2.4165645528
H,0,-1.3343177692,-0.9298076419,2.7958520622

B3PW91/6-31+G*

E(RB3PW91) = -462.335467823

Zero-point correction= 0.187414 (Hartree/Particle)
Thermal correction to Energy= 0.197639
Thermal correction to Enthalpy= 0.198583
Thermal correction to Gibbs Free Energy= 0.152386
Sum of electronic and ZPE= -462.148054
Sum of electronic and thermal Energies= -462.137829
Sum of electronic and thermal Enthalpies= -462.136884
Sum of electronic and thermal Free Energies= -462.183082

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	124.020	38.530	97.230

C,0,-0.034413546,0.1445177289,0.0048690551
C,0,-0.1555664896,0.1040619438,1.3383481367
H,0,0.9019340356,0.3523472925,-0.5046872184
O,0,-1.0334800195,-0.0700433961,-0.9053022062
C,0,-2.8617678474,1.3517989344,-0.1989548806
O,0,-2.2556528348,2.3567594922,-0.4761276842
H,0,-3.8895747558,1.404049404,0.2329644415
C,0,1.0091177467,0.3928927314,2.2392174693
H,0,1.9171290213,0.6177049911,1.668969992
H,0,1.227604416,-0.4589829612,2.8988578699
H,0,0.8046151662,1.2551289659,2.8901518483
C,0,-2.3595956511,-0.0793702192,-0.4003374019
C,0,-3.2281020138,-0.7328499956,-1.4750141377
H,0,-2.9336555903,-1.7803701311,-1.5965017003
H,0,-4.2882619492,-0.6994502751,-1.2006011971
H,0,-3.0945140992,-0.2209075546,-2.4332767954
C,0,-2.4364514301,-0.8326700993,0.9367270602
H,0,-2.1587424491,-1.8757245947,0.7402757521

H,0,-3.4711628344,-0.836125882,1.3013156306
C,0,-1.4845388246,-0.2197451967,1.9656102317
H,0,-1.9254938606,0.6872253617,2.4116649013
H,0,-1.3459141902,-0.9205045401,2.801146833

B3PW91/6-31+G**

E(RB3PW91) = -462.350879166

Zero-point correction= 0.186690 (Hartree/Particle)
Thermal correction to Energy= 0.196939
Thermal correction to Enthalpy= 0.197883
Thermal correction to Gibbs Free Energy= 0.151653
Sum of electronic and ZPE= -462.164189
Sum of electronic and thermal Energies= -462.153940
Sum of electronic and thermal Enthalpies= -462.152996
Sum of electronic and thermal Free Energies= -462.199227

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	123.581	38.689	97.301

C,0,-0.033861674,0.1560481043,0.0084630373
C,0,-0.1586419372,0.1114177326,1.3414363229
H,0,0.9029846844,0.37254062,-0.4953427583
O,0,-1.0294571138,-0.0649398373,-0.9043878594
C,0,-2.8678659117,1.3439666224,-0.1983565529
O,0,-2.2659177684,2.3527015337,-0.4713352583
H,0,-3.896923829,1.3873105867,0.2313802691
C,0,1.0005664321,0.4073658024,2.2463793853
H,0,1.9068668232,0.6415005995,1.67963738
H,0,1.2234753269,-0.444121031,2.9031121034
H,0,0.7861002719,1.2649665459,2.8982795895
C,0,-2.3567244195,-0.0838473558,-0.4027133385
C,0,-3.2184927535,-0.7396765795,-1.4811769932
H,0,-2.9183246528,-1.7844437297,-1.6022697805
H,0,-4.27845419,-0.7114487268,-1.2097409277
H,0,-3.0833699224,-0.2256555512,-2.4368582408
C,0,-2.4318377637,-0.8407037374,0.9323634515
H,0,-2.1472973943,-1.8804250041,0.7330188566
H,0,-3.4667535035,-0.8516254131,1.2933842677
C,0,-1.4863755887,-0.2242090492,1.9644941194
H,0,-1.9330993889,0.6781761019,2.4118249244
H,0,-1.3430837271,-0.9251562343,2.7977240025

B3LYP/6-31G*
E(RB3LYP) = -462.493749741

Zero-point correction= 0.187414 (Hartree/Particle)
Thermal correction to Energy= 0.197631
Thermal correction to Enthalpy= 0.198575
Thermal correction to Gibbs Free Energy= 0.152370
Sum of electronic and ZPE= -462.306336
Sum of electronic and thermal Energies= -462.296119
Sum of electronic and thermal Enthalpies= -462.295175
Sum of electronic and thermal Free Energies= -462.341380

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	124.015	38.483	97.247

C,0,-0.0344074684,0.1518204016,0.0099589264
C,0,-0.1519616274,0.1064479279,1.3422148363
H,0,0.9020735589,0.3572204062,-0.4996454584
O,0,-1.0353900778,-0.0606318782,-0.9040976587
C,0,-2.8722428122,1.3610856302,-0.2125986826
O,0,-2.2413689956,2.3605672771,-0.4535868694
H,0,-3.9180618792,1.4143519094,0.1753423599
C,0,1.019779014,0.3847681422,2.2431165219
H,0,1.9278087253,0.6031774554,1.6709097448
H,0,1.2336480957,-0.4693640205,2.9016062564
H,0,0.8258971916,1.2463981909,2.8982231109
C,0,-2.3692915963,-0.0761153292,-0.4015724775
C,0,-3.2244696416,-0.7463404305,-1.4830105647
H,0,-2.9219250308,-1.7921106477,-1.5950686252
H,0,-4.2877345673,-0.7172334664,-1.2216867792
H,0,-3.0826485272,-0.2394824121,-2.4425268731
C,0,-2.4476316016,-0.8245449422,0.9442953602
H,0,-2.1792933214,-1.8705098745,0.7536732948
H,0,-3.4807870782,-0.8177612447,1.3120538068
C,0,-1.4854568261,-0.2130788392,1.9733692009
H,0,-1.9228828657,0.6949494958,2.4192805478
H,0,-1.3501406685,-0.9138717516,2.8090660216

B3LYP/6-31+G**
E(RB3LYP) = -462.527652524

Zero-point correction= 0.186155 (Hartree/Particle)

Thermal correction to Energy= 0.196404
Thermal correction to Enthalpy= 0.197348
Thermal correction to Gibbs Free Energy= 0.151109
Sum of electronic and ZPE= -462.341498
Sum of electronic and thermal Energies= -462.331248
Sum of electronic and thermal Enthalpies= -462.330304
Sum of electronic and thermal Free Energies= -462.376543

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	123.246	38.748	97.319

C,0,-0.0294557021,0.1735099896,0.0061848834
C,0,-0.1467184182,0.1145391099,1.3398214273
H,0,0.9016755191,0.3977221559,-0.5034578979
O,0,-1.0353115849,-0.0428532496,-0.9063411847
C,0,-2.8996095534,1.3478133539,-0.1970503431
O,0,-2.3066608418,2.3664769637,-0.4623035984
H,0,-3.9317508865,1.3792871603,0.2246579674
C,0,1.0197292288,0.4039680063,2.2456967671
H,0,1.9233616885,0.6448077746,1.6771060817
H,0,1.2461957649,-0.454051213,2.8931289167
H,0,0.8068163318,1.2547922936,2.9074736561
C,0,-2.3692744984,-0.0780859435,-0.4017953952
C,0,-3.222933307,-0.7469508247,-1.4860263428
H,0,-2.9071020223,-1.78690447,-1.6088943699
H,0,-4.283675682,-0.7343334567,-1.2158310462
H,0,-3.0941776708,-0.2291071328,-2.4407032541
C,0,-2.4322275976,-0.8416111248,0.9366567074
H,0,-2.1495760057,-1.8806026972,0.732018683
H,0,-3.4635890092,-0.8534728025,1.3073423863
C,0,-1.4751640754,-0.2289255026,1.9694863678
H,0,-1.9202327425,0.6698358651,2.425643615
H,0,-1.3268069353,-0.9361122555,2.7965019729

BP86/6-31G*

E(RB-P86) = -462.485075693

Zero-point correction= 0.181507 (Hartree/Particle)
Thermal correction to Energy= 0.192019
Thermal correction to Enthalpy= 0.192963
Thermal correction to Gibbs Free Energy= 0.146186
Sum of electronic and ZPE= -462.303569
Sum of electronic and thermal Energies= -462.293057

Sum of electronic and thermal Enthalpies= -462.292113
Sum of electronic and thermal Free Energies= -462.338890

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	120.494	39.729	98.451

C,0,-0.0316533611,0.1722762955,-0.0010136512
C,0,-0.1488089098,0.1197880854,1.3429880847
H,0,0.9106239398,0.391411569,-0.5144854761
O,0,-1.0323557281,-0.0470023954,-0.9250851102
C,0,-2.8886409266,1.3515687338,-0.1902844777
O,0,-2.2733547483,2.3712718837,-0.4387004007
H,0,-3.9383279718,1.3810742345,0.2267853538
C,0,1.0249621053,0.4106571255,2.2427493824
H,0,1.9357795459,0.644721849,1.6640976304
H,0,1.2553335843,-0.4487722441,2.9042063395
H,0,0.8227680703,1.2745278047,2.9077713967
C,0,-2.3705171913,-0.0841330719,-0.4040206729
C,0,-3.2329570301,-0.7492727028,-1.4897771182
H,0,-2.9313678115,-1.8039997471,-1.6084813352
H,0,-4.3030981611,-0.718702054,-1.2203513383
H,0,-3.0939844385,-0.2332108425,-2.4546697635
C,0,-2.4328290081,-0.8504085878,0.938352073
H,0,-2.142087672,-1.8975542765,0.7339628435
H,0,-3.4751452165,-0.8666469553,1.3074851718
C,0,-1.479597562,-0.2249683703,1.974301604
H,0,-1.9392833787,0.6796179273,2.428749027
H,0,-1.3319461299,-0.9325022611,2.8147364373

BP86/6-31+G**
E(RB-P86) = -462.517149748

Zero-point correction= 0.180371 (Hartree/Particle)
Thermal correction to Energy= 0.190915
Thermal correction to Enthalpy= 0.191859
Thermal correction to Gibbs Free Energy= 0.145063
Sum of electronic and ZPE= -462.336779
Sum of electronic and thermal Energies= -462.326235
Sum of electronic and thermal Enthalpies= -462.325291
Sum of electronic and thermal Free Energies= -462.372086

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K

Total 119.801 40.023 98.490

C,0,-0.0229317631,0.1616779205,-0.0028219338
C,0,-0.1447761395,0.114002105,1.3425811077
H,0,0.9187062957,0.3781939468,-0.5162548463
O,0,-1.0294242977,-0.0574582416,-0.9256153038
C,0,-2.888103699,1.3522286529,-0.1923374932
O,0,-2.2874488582,2.3766342584,-0.4658084165
H,0,-3.9257948034,1.3852023558,0.2485073762
C,0,1.02550704,0.4087798756,2.2472232544
H,0,1.9373147413,0.6424519822,1.6721361052
H,0,1.2519535427,-0.4491307429,2.9097853463
H,0,0.8162254072,1.2738842583,2.9064068972
C,0,-2.3695834254,-0.0837134557,-0.4056633884
C,0,-3.2386759289,-0.7438109617,-1.4894284032
H,0,-2.94242536,-1.7993745158,-1.6061019979
H,0,-4.3070311058,-0.7075916201,-1.2168558055
H,0,-3.0986672537,-0.2297962798,-2.4542122014
C,0,-2.4330258216,-0.8487755019,0.937815423
H,0,-2.1445871312,-1.8954921632,0.7316283175
H,0,-3.4745886128,-0.8631310991,1.3066201566
C,0,-1.4776691302,-0.225654599,1.9727808945
H,0,-1.9310549621,0.6821759804,2.4256966532
H,0,-1.3304067343,-0.9315601551,2.8132342582

BB1K/6-31+G**

E(RB+HF-B95) = -462.290760686

Zero-point correction= 0.191389 (Hartree/Particle)
Thermal correction to Energy= 0.201423
Thermal correction to Enthalpy= 0.202367
Thermal correction to Gibbs Free Energy= 0.156707
Sum of electronic and ZPE= -462.099371
Sum of electronic and thermal Energies= -462.089338
Sum of electronic and thermal Enthalpies= -462.088394
Sum of electronic and thermal Free Energies= -462.134054

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	126.395	37.819	96.100

C,0,-0.0518331289,0.1255390482,-0.0025936798
C,0,-0.1806077768,0.1044609365,1.3195235625

H,0,0.8798914558,0.3436565212,-0.5003461605
O,0,-1.0383062878,-0.1196134412,-0.9016815684
C,0,-2.789562152,1.3252254251,-0.1506610543
O,0,-2.1319833042,2.2966992599,-0.3813825615
H,0,-3.8080939875,1.4114309641,0.2743630741
C,0,0.9635923352,0.4334346998,2.2168626149
H,0,1.8629799538,0.6634063231,1.6510363515
H,0,1.1904480716,-0.3948978237,2.8890948604
H,0,0.7348578766,1.2982126748,2.8412092448
C,0,-2.3463305417,-0.1048007757,-0.3954882769
C,0,-3.2359062644,-0.7117092624,-1.4603491353
H,0,-2.9762667486,-1.7585258766,-1.5939339691
H,0,-4.2837838911,-0.6474898631,-1.1758669117
H,0,-3.093406083,-0.195798478,-2.4059569719
C,0,-2.4234129337,-0.8659168554,0.9224067453
H,0,-2.1236692181,-1.8934199055,0.7201113245
H,0,-3.4530453458,-0.8894655056,1.2765700016
C,0,-1.4961525536,-0.234087981,1.9441379568
H,0,-1.9499125011,0.6674564979,2.3686557361
H,0,-1.3459849748,-0.9140545823,2.7836048171

M06/6-31G*

E(RM06) = -462.186608722
Zero-point correction= 0.187053 (Hartree/Particle)
Thermal correction to Energy= 0.197059
Thermal correction to Enthalpy= 0.198003
Thermal correction to Gibbs Free Energy= 0.152475
Sum of electronic and ZPE= -461.999556
Sum of electronic and thermal Energies= -461.989550
Sum of electronic and thermal Enthalpies= -461.988606
Sum of electronic and thermal Free Energies= -462.034133

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	123.656	38.313	95.821

C,0,-0.0400864791,0.1404324164,-0.0006846168
C,0,-0.167441058,0.1082117778,1.3284286158
H,0,0.9030407334,0.352774864,-0.5015524865
O,0,-1.0309366003,-0.0881301754,-0.9087528206
C,0,-2.8316050578,1.3385559608,-0.183824115
O,0,-2.2096212327,2.3344751721,-0.436069264
H,0,-3.8701568032,1.3818390491,0.2412028642

C,0,0.9835470717,0.4108750055,2.2297317935
H,0,1.8950312807,0.6381639759,1.6630526874
H,0,1.2048769095,-0.4332449262,2.900804445
H,0,0.7705258341,1.2769171606,2.8752719971
C,0,-2.349407433,-0.0894820888,-0.398196733
C,0,-3.2251181704,-0.7257485294,-1.4639310265
H,0,-2.933801158,-1.7738499809,-1.6013527696
H,0,-4.2836736277,-0.6919931432,-1.175828712
H,0,-3.1009129122,-0.2026772503,-2.4194453499
C,0,-2.4282631555,-0.844298303,0.9286887485
H,0,-2.1386190617,-1.8862713332,0.7280269236
H,0,-3.4688013513,-0.8590327409,1.2837952356
C,0,-1.4895930744,-0.2218460456,1.9543523172
H,0,-1.9404257644,0.6862093758,2.3953282212
H,0,-1.3450468899,-0.9121382409,2.8002700447

M06/6-31+G**

E(RM06) = -462.215674075

Zero-point correction= 0.185871 (Hartree/Particle)
Thermal correction to Energy= 0.195921
Thermal correction to Enthalpy= 0.196865
Thermal correction to Gibbs Free Energy= 0.151263
Sum of electronic and ZPE= -462.029803
Sum of electronic and thermal Energies= -462.019753
Sum of electronic and thermal Enthalpies= -462.018809
Sum of electronic and thermal Free Energies= -462.064411

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	122.942	38.581	95.977

C,0,-0.033141784,0.136430457,-0.0020229385
C,0,-0.1653535972,0.105327084,1.3283435563
H,0,0.9086362355,0.3531517613,-0.5004170899
O,0,-1.0275104012,-0.0962980154,-0.9091113273
C,0,-2.8313484983,1.335876644,-0.1816231873
O,0,-2.2280106458,2.3367947032,-0.4651584168
H,0,-3.854153803,1.3805309322,0.2759940254
C,0,0.9793884543,0.4173067018,2.235629587
H,0,1.8896712318,0.6536261893,1.673734078
H,0,1.2028908267,-0.4257966398,2.9046203344
H,0,0.7517800754,1.2800342341,2.8781582989

C,0,-2.3476429597,-0.0918629983,-0.3993269862
C,0,-3.2277944177,-0.7207712845,-1.4662364826
H,0,-2.9396945136,-1.7684565333,-1.6041536393
H,0,-4.2844911935,-0.6838416206,-1.1764626642
H,0,-3.1011238131,-0.1965613409,-2.4194274586
C,0,-2.4253449597,-0.850449941,0.9254951299
H,0,-2.133535602,-1.8897514316,0.7200936112
H,0,-3.4647722014,-0.8686377502,1.2799435556
C,0,-1.4878024389,-0.228415003,1.9520409215
H,0,-1.9371801449,0.6793449007,2.3929623073
H,0,-1.3399538498,-0.9178390492,2.796240785

MP2/6-31G*
-0.1390598291D+01 EUMP2

Zero-point correction= 0.190904 (Hartree/Particle)
Thermal correction to Energy= 0.200923
Thermal correction to Enthalpy= 0.201867
Thermal correction to Gibbs Free Energy= 0.156200
Sum of electronic and ZPE= -460.823605
Sum of electronic and thermal Energies= -460.813586
Sum of electronic and thermal Enthalpies= -460.812642
Sum of electronic and thermal Free Energies= -460.858309

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	126.081	37.847	96.114

C,0,-0.0438216222,0.1282167545,-0.0072452365
C,0,-0.1786670768,0.1062404537,1.3288675157
H,0,0.8942326535,0.3420520186,-0.5118356475
O,0,-1.0370766765,-0.1282921254,-0.9257050375
C,0,-2.7912038144,1.3330884292,-0.152795381
O,0,-2.1130556617,2.3151981912,-0.4050829213
H,0,-3.8136273384,1.4323233582,0.277562662
C,0,0.9739977547,0.4410545485,2.2282690011
H,0,1.8768670224,0.6670476623,1.6530606343
H,0,1.2012545923,-0.3896663404,2.9069636637
H,0,0.7455824283,1.3146289215,2.8507297016
C,0,-2.3611120271,-0.1076241415,-0.3942461988
C,0,-3.2487590808,-0.7170754457,-1.4702037388
H,0,-2.967029788,-1.7624577192,-1.6195281132
H,0,-4.3027232787,-0.6721786076,-1.1797737326
H,0,-3.1115471938,-0.1778486776,-2.4111966956

C,0,-2.4281711828,-0.8776330571,0.9262344165
H,0,-2.1123678513,-1.9066873788,0.7200454617
H,0,-3.4643616461,-0.9159836796,1.2837212354
C,0,-1.5010608245,-0.233927119,1.9563158237
H,0,-1.9651330317,0.6683237264,2.3841124084
H,0,-1.3487043563,-0.9190577721,2.8010461788

MPW1K/6-31+G**

E(RmPW+HF-PW91) = -462.396687990

Zero-point correction= 0.192342 (Hartree/Particle)
Thermal correction to Energy= 0.202396
Thermal correction to Enthalpy= 0.203340
Thermal correction to Gibbs Free Energy= 0.157340
Sum of electronic and ZPE= -462.204346
Sum of electronic and thermal Energies= -462.194292
Sum of electronic and thermal Enthalpies= -462.193348
Sum of electronic and thermal Free Energies= -462.239348

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	127.005	37.655	96.815

C,0,-0.0469437748,0.4752862822,0.1920081709
C,0,-0.1285896949,-0.0337535445,1.4196833038
H,0,0.8917551044,0.6447615638,-0.313646894
O,0,-1.0983080635,0.8553057987,-0.5808202202
C,0,-2.411918522,-1.1124401524,-0.5509956202
O,0,-3.2038211316,-1.8888971906,-0.0960796317
H,0,-1.685760023,-1.4099894732,-1.3266161848
C,0,1.0959605659,-0.454918564,2.1629182166
H,0,1.9978516212,-0.3059458222,1.5733362068
H,0,1.0449794637,-1.5103500706,2.4344601346
H,0,1.203204378,0.1074485665,3.091491335
C,0,-2.3564213785,0.3582005065,-0.1649018937
C,0,-3.3991720901,1.0986484027,-0.9798388228
H,0,-4.3926221435,0.7258146201,-0.7452056068
H,0,-3.349724896,2.1601441953,-0.7490810459
H,0,-3.2167115281,0.972879152,-2.0450084701
C,0,-2.5479778418,0.5394205128,1.3315685927
H,0,-3.5310107559,0.1683053396,1.6105345119
H,0,-2.5197661026,1.6090822149,1.5375735196
C,0,-1.4530848232,-0.1797278257,2.1027030647

H,0,-1.3852781462,0.2245569986,3.1143311539
H,0,-1.7000202176,-1.2374765104,2.2191741798

MPWLYP/6-31+G**
E(RmPW-LYP) = -462.331955292

Zero-point correction= 0.180187 (Hartree/Particle)
Thermal correction to Energy= 0.190903
Thermal correction to Enthalpy= 0.191847
Thermal correction to Gibbs Free Energy= 0.144229
Sum of electronic and ZPE= -462.151768
Sum of electronic and thermal Energies= -462.141052
Sum of electronic and thermal Enthalpies= -462.140108
Sum of electronic and thermal Free Energies= -462.187726

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	119.794	40.225	100.221

C,0,-0.1855715339,0.848108822,0.2899574002
C,0,-0.2027308924,0.0514380422,1.3825494175
H,0,0.7056654827,1.3736704704,-0.0603985459
O,0,-1.2622106585,1.1322503257,-0.5398032346
C,0,-3.6046901889,1.2191533328,-0.8838733815
O,0,-4.7163894799,0.8025406113,-1.183382195
H,0,-3.3439511201,2.3059105971,-0.9445208081
C,0,1.0524239287,-0.2086445505,2.1882680316
H,0,1.924477932,0.3152724185,1.7655780492
H,0,1.2938740561,-1.2876941154,2.2211651246
H,0,0.9340058392,0.1211933949,3.237055665
C,0,-2.4698944968,0.3232697792,-0.3548564907
C,0,-2.3597439526,-0.9770106262,-1.177209921
H,0,-1.5570697287,-1.6196772345,-0.7882538496
H,0,-3.3145065669,-1.522572683,-1.1376033979
H,0,-2.1363468938,-0.74044286,-2.2283656341
C,0,-2.7220661063,0.0781641796,1.1629066507
H,0,-3.6353841184,-0.5263940433,1.2760426199
H,0,-2.9076944323,1.0522348814,1.6481910667
C,0,-1.5007232606,-0.5978228561,1.8291547673
H,0,-1.6001181687,-0.5195946084,2.9275437727
H,0,-1.4878436401,-1.6836112777,1.6091708929

O3LYP/6-31+G**
E(RO3LYP) = -462.358285886

Zero-point correction= 0.186082 (Hartree/Particle)
Thermal correction to Energy= 0.196343
Thermal correction to Enthalpy= 0.197287
Thermal correction to Gibbs Free Energy= 0.151029
Sum of electronic and ZPE= -462.172204
Sum of electronic and thermal Energies= -462.161943
Sum of electronic and thermal Enthalpies= -462.160999
Sum of electronic and thermal Free Energies= -462.207257

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	123.207	38.858	97.358

C,0,-0.0296563894,0.1546959801,0.0152068189
C,0,-0.1471132584,0.103308129,1.3518692666
H,0,0.9070614373,0.3570689435,-0.4949161067
O,0,-1.0311378487,-0.041555005,-0.8981301956
C,0,-2.8994374049,1.3658923946,-0.2272309904
O,0,-2.3154797169,2.3820948381,-0.5183892855
H,0,-3.9322148036,1.399742791,0.1952965822
C,0,1.0228286505,0.3718028522,2.2556354575
H,0,1.9320027338,0.5921459895,1.6888528608
H,0,1.2326786532,-0.4871063487,2.9068043765
H,0,0.8284444214,1.228834083,2.9145475817
C,0,-2.3646275029,-0.0660870613,-0.4026567038
C,0,-3.2122253372,-0.7447949087,-1.4863767687
H,0,-2.8946724289,-1.7845157756,-1.6012257572
H,0,-4.2740682211,-0.7334492833,-1.2242201696
H,0,-3.0801650647,-0.234443365,-2.4441317875
C,0,-2.4422872892,-0.8135870663,0.94262426
H,0,-2.1764995398,-1.8586116417,0.7498361166
H,0,-3.474040413,-0.8078365347,1.3102064971
C,0,-1.4817782704,-0.2133645556,1.9742614786
H,0,-1.9128830592,0.6919104397,2.4291429328
H,0,-1.3512173477,-0.9224028946,2.8023095357

PW91/6-31+G**
E(RPW91-PW91) = -462.345150556

Zero-point correction= 0.181302 (Hartree/Particle)
Thermal correction to Energy= 0.191804
Thermal correction to Enthalpy= 0.192748

Thermal correction to Gibbs Free Energy= 0.146039
Sum of electronic and ZPE= -462.163849
Sum of electronic and thermal Energies= -462.153346
Sum of electronic and thermal Enthalpies= -462.152402
Sum of electronic and thermal Free Energies= -462.199111

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	120.359	39.854	98.308

C,0,-0.0231772208,0.1390949712,-0.000067483
C,0,-0.1503235032,0.1038031684,1.3430318779
H,0,0.9208924609,0.3420018204,-0.5098406799
O,0,-1.0265102511,-0.0774461284,-0.9213603347
C,0,-2.8612524159,1.3571103722,-0.1999074552
O,0,-2.2422796994,2.3683581267,-0.4719705597
H,0,-3.8975706887,1.4083335159,0.2352671603
C,0,1.015217487,0.3957327734,2.2482372917
H,0,1.930041191,0.6145848614,1.6768515088
H,0,1.2292708652,-0.4556345528,2.9190585265
H,0,0.8107640991,1.2673671102,2.8960838515
C,0,-2.3644874416,-0.0834716058,-0.406308732
C,0,-3.2388082847,-0.7352198641,-1.4850464221
H,0,-2.9573343139,-1.7930483469,-1.5954054765
H,0,-4.3045440482,-0.6827806203,-1.2148560679
H,0,-3.08981074,-0.2292168046,-2.4500750433
C,0,-2.4404659596,-0.8378042288,0.938282476
H,0,-2.1609446131,-1.8860389066,0.7398345192
H,0,-3.4812470245,-0.8403395258,1.3021914072
C,0,-1.4854496868,-0.2172744959,1.9692084897
H,0,-1.9304607048,0.6971500406,2.4116055952
H,0,-1.3480075069,-0.9155196803,2.8145015504

G4

G4 -0.2232786423D+01 EUMP2

Zero-point correction= 0.185885 (Hartree/Particle)
Thermal correction to Energy= 0.196282
Thermal correction to Enthalpy= 0.197226
Thermal correction to Gibbs Free Energy= 0.150328
Sum of electronic and ZPE= -462.345113
Sum of electronic and thermal Energies= -462.334716
Sum of electronic and thermal Enthalpies= -462.333771

Sum of electronic and thermal Free Energies= -462.380669

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	123.169	38.866	98.705

C,0,-0.0052927302,-0.0061910164,-0.0008868121
C,0,-0.0004442441,0.0000820911,1.3340266981
H,0,0.9030187048,-0.0064131969,-0.5949914472
O,0,-1.1036063278,-0.0062092563,-0.8128343503
C,0,-3.3877981315,0.414307002,-1.1196164832
O,0,-4.5553805139,0.1295033962,-1.1561668498
H,0,-2.9481159785,1.2206583813,-1.7469294991
C,0,1.2833150297,-0.0348477932,2.1131193439
H,0,2.1551553043,-0.0685159981,1.4532084375
H,0,1.3297419918,-0.9129656583,2.7713203466
H,0,1.3842034753,0.8460068465,2.7609263256
C,0,-2.3737296767,-0.2489627232,-0.1891850601
C,0,-2.6374584515,-1.7519978854,-0.0822585209
H,0,-3.6705908807,-1.919823474,0.2304624473
H,0,-2.4899741337,-2.2258933143,-1.0560995516
H,0,-1.9602704006,-2.2211534447,0.6345375749
C,0,-2.4519958775,0.4809632522,1.1693534117
H,0,-3.4296261791,0.2874401085,1.6192625313
H,0,-2.384214982,1.5600520166,0.9864435125
C,0,-1.3028329542,0.0529545523,2.0912599991
H,0,-1.2224232179,0.7642313553,2.9234299746
H,0,-1.5199857903,-0.9188629916,2.5572291983

VRI on the B3PW91/6-31+G surface**

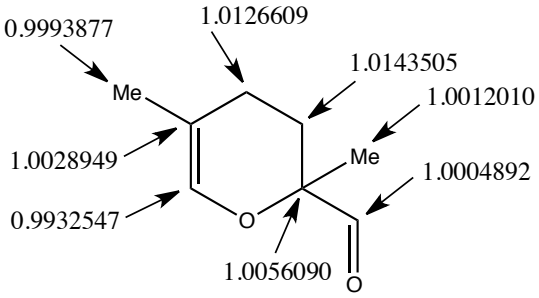
C	-1.544054	0.254805	0.3862
C	-1.072393	-0.971234	0.975292
O	0.027958	-1.038241	1.543748
H	-1.69875	-1.872768	0.850407
C	-0.71735	1.387308	0.585606
H	-1.156944	2.352407	0.33407
H	-0.15885	1.37694	1.52062
C	1.544054	0.254805	-0.3862
C	1.072393	-0.971234	-0.975292
H	1.69875	-1.872768	-0.850406
O	-0.027957	-1.038242	-1.543748
C	0.717349	1.387308	-0.585607
H	1.156944	2.352407	-0.334071
H	0.15885	1.376939	-1.520621

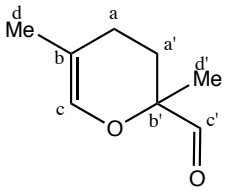
C	-2.752507	0.269967	-0.49099
H	-2.45299	0.337188	-1.545686
H	-3.329945	-0.653182	-0.381193
H	-3.407942	1.120268	-0.273348
C	2.752507	0.269968	0.49099
H	2.45299	0.337189	1.545686
H	3.329944	-0.653181	0.381194
H	3.407942	1.120268	0.273347

B.2 Calculated Equlibrium Isotope Effects for methacrolein dimerization

The equilibrium isotope effects were calculated based on the B3PW91/6-31+G** product structure by the method of Bigeleisen and Mayer, employing a locally modified version of the program QUIVER (the changes do not affect the basic algorithm but make the program easier to use and make it easier to verify its results). Frequencies were scaled by 0.9614. The exact choice of scaling factor makes little difference in the isotope effects.

The figure below at left shows the reduced isotopic partition functions obtained from QUIVER. These numbers are a measure of the preference for ^{13}C in a position if the atoms were in equilibrium with free atoms in space. Equilibrium isotope effects are determined from their ratio. While the particular values of the reduced isotopic partition functions vary significantly for differing theoretical levels, their ratio does not. For example, the corresponding EIEs at B3LYP/6-31G* differ by at most 0.00021.





Intramolecular EIE at 70 ^{0}C

a/a' 0.998
b/b' 0.997
c/c' 0.993
d/d' 0.998

B.3 Located structures and energies for the dimerization of cyclopentadienone

Transition Structures for dimerization cyclopentadienone

G4

-0.2602556095D+01 EUMP2

Zero-point correction= 0.150414 (Hartree/Particle)

Thermal correction to Energy= 0.159817
Thermal correction to Enthalpy= 0.160761
Thermal correction to Gibbs Free Energy= 0.116348
Sum of electronic and ZPE= -536.091626
Sum of electronic and thermal Energies= -536.082223
Sum of electronic and thermal Enthalpies= -536.081279
Sum of electronic and thermal Free Energies= -536.125692

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	100.287	37.150	93.475

C,0,0.0001735526,-0.000145841,-0.0000546169
C,0,-0.0000119895,-0.0003435467,1.4916852693
C,0,1.2976350236,-0.000082284,1.9107925782
C,0,2.1908480141,-0.1894019359,0.7958901181
C,0,1.4390138752,-0.3318530653,-0.3629857848
C,0,0.1431610318,-2.6664640633,0.6858165462
H,0,-0.8902673404,0.1361024989,2.0883449197
H,0,1.6310347946,0.0923346771,2.93681903
H,0,3.2691170385,-0.171200751,0.858169596
C,0,0.8960689874,-2.4226935893,-0.4553433118
H,0,1.8167944718,-0.2648398154,-1.3737568346
H,0,0.5192332746,-2.4005528806,-1.4684433584
H,0,-0.9351648164,-2.690026824,0.7452494235
C,0,1.035342394,-2.953122386,1.7805851497
C,0,2.3333794107,-2.9160625654,1.3643337254
H,0,0.7009903767,-3.1353879914,2.7941997508
H,0,3.2230839304,-3.1044819657,1.9475136709
C,0,2.3345840748,-2.785088189,-0.1216448153
O,0,3.2441962813,-2.9661761612,-0.8952430447
O,0,-0.9087247524,0.2483018801,-0.7555802892

M06/6-31G*
E(RM06) = -535.846767124

Zero-point correction= 0.150492 (Hartree/Particle)
Thermal correction to Energy= 0.159963
Thermal correction to Enthalpy= 0.160907
Thermal correction to Gibbs Free Energy= 0.115820
Sum of electronic and ZPE= -535.696275
Sum of electronic and thermal Energies= -535.686804
Sum of electronic and thermal Enthalpies= -535.685860
Sum of electronic and thermal Free Energies= -535.730948

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	100.378	37.482	94.894

C,0,-0.5129729912,-0.028395806,1.7898127143
C,0,0.9724075697,0.0140393634,1.8585583932
C,0,1.3968591945,1.0280552875,1.0597970634
C,0,0.2907068141,1.5846223204,0.3171391136
C,0,-0.856330143,0.8909549593,0.6401686999
C,0,0.2918588016,-1.5843934166,-0.317193514
H,0,1.5582701007,-0.5880640994,2.5442914266
H,0,2.4242679272,1.3655764074,0.9504201303
H,0,0.3605021423,2.4269033329,-0.3636255325
C,0,-0.8557771032,-0.8916092892,-0.639991107
H,0,-1.8742220888,1.180860297,0.3963713264
H,0,-1.8733950014,-1.1822950409,-0.395980177
H,0,0.3624406158,-2.4266184316,0.3635592916
C,0,1.3974299403,-1.0269861885,-1.0600894758
C,0,0.9720338697,-0.0133061782,-1.8587732329
H,0,2.4251196723,-1.3637193073,-0.9509235042
H,0,1.5572911482,0.5892404474,-2.5446337558
C,0,-0.5133644644,0.027993439,-1.7897142696
O,0,-1.2852317323,0.6357940949,-2.4964849359
O,0,-1.284225272,-0.6367941914,2.4967403452

M06/6-31G**

E(RM06) = -535.858637612

Zero-point correction= 0.150334 (Hartree/Particle)
Thermal correction to Energy= 0.159806
Thermal correction to Enthalpy= 0.160750
Thermal correction to Gibbs Free Energy= 0.115674
Sum of electronic and ZPE= -535.708303
Sum of electronic and thermal Energies= -535.698832
Sum of electronic and thermal Enthalpies= -535.697888
Sum of electronic and thermal Free Energies= -535.742963

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	100.280	37.535	94.870

C,0,-0.5130220134,-0.0287225529,1.7907054309
C,0,0.9723889147,0.0130720664,1.8585218907

C,0,1.3964355889,1.0268627859,1.0592576466
C,0,0.2909461283,1.5826448708,0.3163508893
C,0,-0.8564610169,0.8884252029,0.6390377562
C,0,0.2920968231,-1.5824154558,-0.3164048991
H,0,1.5585716633,-0.5884763392,2.5423148293
H,0,2.4227804874,1.3633055818,0.9497909858
H,0,0.3605488494,2.423089913,-0.3645414283
C,0,-0.8559095829,-0.8890793045,-0.6388599438
H,0,-1.8727434287,1.1802586444,0.3960948799
H,0,-1.8719167025,-1.181691748,-0.3957038392
H,0,0.3624846454,-2.4228042498,0.3644761037
C,0,1.397005576,-1.0257940541,-1.0595499224
C,0,0.9720145639,-0.0123393315,-1.858737158
H,0,2.4236306812,-1.3614496231,-0.9502940096
H,0,1.5575929834,0.5896517988,-2.5426582053
C,0,-0.5134137889,0.0283200357,-1.7906071657
O,0,-1.2851837295,0.6350112942,-2.4981958408
O,0,-1.2841776422,-0.6360115351,2.4984509998

M06/6-31+G*
E(RM06) = -535.867220245

Zero-point correction= 0.150194 (Hartree/Particle)
Thermal correction to Energy= 0.159691
Thermal correction to Enthalpy= 0.160635
Thermal correction to Gibbs Free Energy= 0.115463
Sum of electronic and ZPE= -535.717027
Sum of electronic and thermal Energies= -535.707530
Sum of electronic and thermal Enthalpies= -535.706585
Sum of electronic and thermal Free Energies= -535.751758

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	100.207	37.510	95.073

C,0,-0.5093463305,-0.0269258576,1.7935916303
C,0,0.9741854036,0.0197431588,1.8679059276
C,0,1.3972884729,1.0350049442,1.0667590857
C,0,0.2891219872,1.5878239514,0.3224275446
C,0,-0.8570654205,0.8882172991,0.6438717202
C,0,0.2902614711,-1.5876352045,-0.3225226577
H,0,1.5599738399,-0.5816401955,2.5550690432
H,0,2.4238164807,1.3774288209,0.9608407584
H,0,0.3558277438,2.4323576156,-0.3567812778

C,0,-0.856527692,-0.8888969053,-0.6437094422
H,0,-1.8771117989,1.1756489472,0.4044395885
H,0,-1.8763055798,-1.1771069956,-0.4040668096
H,0,0.3577598063,-2.4321218154,0.3566666196
C,0,1.3978504326,-1.0339407909,-1.0670556722
C,0,0.9738068173,-0.0189721397,-1.8680801045
H,0,2.424663097,-1.3755776731,-0.9613562263
H,0,1.5589937303,0.5828794441,-2.5553458933
C,0,-0.5097461834,0.0265416193,-1.7934786949
O,0,-1.2823928848,0.633853914,-2.5043214643
O,0,-1.2813843927,-0.634824137,2.504595325

M06/6-31+G**

E(RM06) = -535.879057029

Zero-point correction= 0.150010 (Hartree/Particle)
Thermal correction to Energy= 0.159520
Thermal correction to Enthalpy= 0.160464
Thermal correction to Gibbs Free Energy= 0.115272
Sum of electronic and ZPE= -535.729047
Sum of electronic and thermal Energies= -535.719537
Sum of electronic and thermal Enthalpies= -535.718593
Sum of electronic and thermal Free Energies= -535.763785

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	100.100	37.597	95.115

C,0,-0.5093243869,-0.0271458627,1.7949002933
C,0,0.9741885317,0.019560098,1.8693725141
C,0,1.3969165331,1.0347066957,1.067788629
C,0,0.2895122169,1.5861690377,0.3223830708
C,0,-0.8569295413,0.8854372679,0.6427888347
C,0,0.2906514461,-1.5859766098,-0.3224748082
H,0,1.5596229758,-0.5804823578,2.555618679
H,0,2.4221140983,1.3765427761,0.9624179876
H,0,0.3560949513,2.4288989529,-0.3566926591
C,0,-0.8563928001,-0.8861145223,-0.642625263
H,0,-1.8754107144,1.1747707179,0.4046035463
H,0,-1.874603973,-1.1762265197,-0.4042303587
H,0,0.3580242196,-2.4286600054,0.3565809521
C,0,1.397479125,-1.033642222,-1.0680846263
C,0,0.9738100878,-0.0187922003,-1.869550109
H,0,2.4229606811,-1.3746923641,-0.9629316018

H,0,1.5586440689,0.5817168781,-2.5559001633
C,0,-0.5097239625,0.0267605662,-1.7947884255
O,0,-1.2824863486,0.6331571333,-2.5060055469
O,0,-1.2814782089,-0.6341294596,2.5062780548

B3LYP/6-31G*
E(RB3LYP) = -536.203589304

Zero-point correction= 0.150989 (Hartree/Particle)
Thermal correction to Energy= 0.160418
Thermal correction to Enthalpy= 0.161362
Thermal correction to Gibbs Free Energy= 0.116216
Sum of electronic and ZPE= -536.052600
Sum of electronic and thermal Energies= -536.043172
Sum of electronic and thermal Enthalpies= -536.042228
Sum of electronic and thermal Free Energies= -536.087373

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	100.664	37.152	95.017

O,0,-1.2787839589,0.6138619592,-2.5601464968
O,0,-1.2777808732,-0.6148470168,2.5604077989
C,0,-0.5096922552,0.0287041567,-1.823054094
C,0,-0.5092914188,-0.0290993754,1.8231557625
C,0,-0.8629168256,-0.871644103,-0.6496697215
C,0,0.980580709,0.0164421172,1.8777067095
C,0,0.2884970074,-1.5822456372,-0.326336084
C,0,1.3974131168,1.0385778115,1.0717243874
C,0,1.3979867615,-1.0375099514,-1.0720187655
C,0,0.2873509456,1.5824625618,0.3262726251
C,0,0.9802029825,-0.0156947597,-1.8779148244
C,0,-0.8634502785,0.8709779748,0.649845174
H,0,-1.8782352685,-1.1818014429,-0.4351317422
H,0,1.5739753371,-0.5721642949,2.5654500016
H,0,0.3477347126,-2.4346747669,0.3381141812
H,0,2.4197349178,1.3861035348,0.9673314517
H,0,2.420596492,-1.3842513912,-0.9678381846
H,0,0.3457967598,2.4349368789,-0.3381897986
H,0,1.5730030232,0.5733663333,-2.5657815776
H,0,-1.8790508864,1.1803564112,0.4355181972

B3LYP/6-31+G**
E(RB3LYP) = -536.240489059

Zero-point correction= 0.150455 (Hartree/Particle)
Thermal correction to Energy= 0.159907
Thermal correction to Enthalpy= 0.160851
Thermal correction to Gibbs Free Energy= 0.115651
Sum of electronic and ZPE= -536.090034
Sum of electronic and thermal Energies= -536.080582
Sum of electronic and thermal Enthalpies= -536.079638
Sum of electronic and thermal Free Energies= -536.124838

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	100.343	37.244	95.131

O,0,-1.2765099526,0.609849943,-2.5707747579
O,0,-1.2755075883,-0.610833212,2.5710355961
C,0,-0.5059590355,0.0280022873,-1.8278962778
C,0,-0.5055575982,-0.028394535,1.8279971896
C,0,-0.8636675853,-0.865829871,-0.6525935929
C,0,0.9823658757,0.0206056592,1.8878442759
C,0,0.2872445918,-1.5833499819,-0.3314821759
C,0,1.3976157812,1.0440593988,1.0789846735
C,0,1.3981919667,-1.0429912853,-1.0792792718
C,0,0.2860988438,1.5835658317,0.3314185572
C,0,0.9819891025,-0.0198565547,-1.8880525833
C,0,-0.8641958814,0.8651631207,0.6527690821
H,0,-1.8800049201,-1.1751797408,-0.4431329103
H,0,1.5756700606,-0.5658726783,2.5767944859
H,0,0.3433616435,-2.4360736121,0.3323172907
H,0,2.4181798616,1.3961300724,0.97854128
H,0,2.4190466404,-1.3942790125,-0.9790479497
H,0,0.3414238563,2.43633225,-0.3323924756
H,0,1.5747000538,0.567076566,-2.5771261018
H,0,-1.8808137166,1.1737333547,0.4435196658

M062X/6-31G*
E(RM062X) = -535.978502155

Zero-point correction= 0.152642 (Hartree/Particle)
Thermal correction to Energy= 0.161948
Thermal correction to Enthalpy= 0.162892
Thermal correction to Gibbs Free Energy= 0.118014
Sum of electronic and ZPE= -535.825860
Sum of electronic and thermal Energies= -535.816554

Sum of electronic and thermal Enthalpies= -535.815610
Sum of electronic and thermal Free Energies= -535.860488

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	101.624	36.712	94.453

C,0,-0.5166202127,-0.0348353025,1.7969738931
C,0,0.9767540787,-0.0092445431,1.8462540729
C,0,1.3965773345,1.0110205051,1.0516672567
C,0,0.2933275634,1.557352366,0.296509813
C,0,-0.8599601732,0.857248703,0.6163739919
C,0,0.2944609697,-1.5571297762,-0.2965730273
H,0,1.5636245895,-0.6074867239,2.5303909469
H,0,2.4215619136,1.3469517738,0.9405543429
H,0,0.3587622629,2.4072580308,-0.3705536148
C,0,-0.8594299035,-0.8579114799,-0.6161987156
H,0,-1.8728776128,1.1725984415,0.3957073252
H,0,-1.8720592602,-1.1740381771,-0.3953216712
H,0,0.3606858852,-2.4069849906,0.3704766763
C,0,1.3971344869,-1.0099530758,-1.051961098
C,0,0.9763635378,0.0099878962,-1.8464623298
H,0,2.422399492,-1.3450979838,-0.9410608842
H,0,1.5626327278,0.6086790915,-2.5307219651
C,0,-0.5170196032,0.0344341037,-1.7968707876
O,0,-1.2868201012,0.6107586382,-2.5249315838
O,0,-1.2858269751,-0.6117504968,2.5251943586

B3PW91/6-31G*
E(RB3PW91) = -536.000130406

Zero-point correction= 0.151220 (Hartree/Particle)
Thermal correction to Energy= 0.160758
Thermal correction to Enthalpy= 0.161702
Thermal correction to Gibbs Free Energy= 0.116966
Sum of electronic and ZPE= -535.848910
Sum of electronic and thermal Energies= -535.839372
Sum of electronic and thermal Enthalpies= -535.838428
Sum of electronic and thermal Free Energies= -535.883164

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	100.877	37.407	94.155

C,0,0.0412405514,0.0120942953,-0.0282481665
C,0,-0.011057209,-0.0188289397,1.464598259
C,0,1.2691510987,-0.0334762688,1.9224853241
C,0,2.2008322382,-0.1711904243,0.8152663209
C,0,1.4918240488,-0.2516189098,-0.3589419748
C,0,0.1433318409,-2.6956416758,0.6933437187
H,0,-0.9232731071,0.0958315247,2.0364632313
H,0,1.5760005502,0.0226867726,2.9617133784
H,0,3.2795539753,-0.1646348659,0.9150576732
C,0,0.8545945396,-2.5043197656,-0.4665820443
H,0,1.8900684295,-0.2165188443,-1.3653925786
H,0,0.4582939688,-2.4438088977,-1.4725928354
H,0,-0.9355796276,-2.7115296291,0.7899847627
C,0,1.072889779,-2.9377905651,1.784313384
C,0,2.3539795859,-2.9090792486,1.3295684152
H,0,0.7640430113,-3.0921963739,2.8129427352
H,0,3.2651020605,-3.0775223573,1.889744431
C,0,2.3045620986,-2.7983293722,-0.1595837359
O,0,3.2081446053,-2.9669692686,-0.9526212942
O,0,-0.8608271981,0.255241143,-0.803466017

B3PW91/6-31G**

E(RB3PW91) = -536.012337170

Zero-point correction= 0.151026 (Hartree/Particle)
Thermal correction to Energy= 0.160555
Thermal correction to Enthalpy= 0.161499
Thermal correction to Gibbs Free Energy= 0.116801
Sum of electronic and ZPE= -535.861311
Sum of electronic and thermal Energies= -535.851782
Sum of electronic and thermal Enthalpies= -535.850838
Sum of electronic and thermal Free Energies= -535.895536

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	100.750	37.429	94.075

C,0,0.0387894977,0.0108454199,-0.0267279735
C,0,-0.0107523209,-0.0204679254,1.4658539653
C,0,1.2706547535,-0.0343237471,1.9212304505
C,0,2.1998077393,-0.1743026505,0.8138087861
C,0,1.4883184626,-0.2575953717,-0.3598465898
C,0,0.1443588622,-2.6924053799,0.6921897803
H,0,-0.9206137575,0.0939659791,2.0401743308

H,0,1.5783907827,0.0231128903,2.9594243337
H,0,3.2780423493,-0.1676410047,0.9109697509
C,0,0.8581013155,-2.4982847816,-0.466909229
H,0,1.886320084,-0.2194975811,-1.3656649411
H,0,0.4620425595,-2.4408180995,-1.4725743474
H,0,-0.9340604006,-2.7081496141,0.7862031705
C,0,1.071388468,-2.9368277982,1.7831416117
C,0,2.353672128,-2.9075666642,1.3309732595
H,0,0.7616572342,-3.092403341,2.810619
H,0,3.2624353922,-3.076016801,1.8936105454
C,0,2.3070101033,-2.797230468,-0.1579472693
O,0,3.2110882953,-2.9677680412,-0.9498442327
O,0,-0.8637763083,0.2557733086,-0.8006314151

B3PW91/6-31+G*

E(RB3PW91) = -536.018979467

Zero-point correction= 0.150915 (Hartree/Particle)
Thermal correction to Energy= 0.160476
Thermal correction to Enthalpy= 0.161421
Thermal correction to Gibbs Free Energy= 0.116616
Sum of electronic and ZPE= -535.868065
Sum of electronic and thermal Energies= -535.858503
Sum of electronic and thermal Enthalpies= -535.857559
Sum of electronic and thermal Free Energies= -535.902364

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	100.700	37.459	94.300

C,0,0.0402438186,0.0147646714,-0.0251392938
C,0,-0.0126757015,-0.0120105907,1.4664430234
C,0,1.2696851124,-0.0267350212,1.9233656429
C,0,2.2001428882,-0.1663030083,0.8141852165
C,0,1.4882066399,-0.2507224678,-0.3598988608
C,0,0.1440237209,-2.7004046474,0.6918054638
H,0,-0.9252848506,0.1035628365,2.0382404957
H,0,1.5774854883,0.0337069794,2.9624105106
H,0,3.2795620763,-0.1586543195,0.911608617
C,0,0.8582138682,-2.5051217838,-0.4676126334
H,0,1.8826312088,-0.2153903395,-1.3682362676
H,0,0.46573676,-2.4446634052,-1.4755163638
H,0,-0.9355805332,-2.7171562505,0.7859842476
C,0,1.0723546869,-2.9445848589,1.784549604

C,0,2.3555951441,-2.9160419277,1.3307615743
H,0,0.7625577414,-3.1032328999,2.8125890953
H,0,3.2671110827,-3.0853875238,1.890784599
C,0,2.3055530819,-2.801282548,-0.1567401151
O,0,3.2103888903,-2.9750114673,-0.9507181905
O,0,-0.8630758835,0.2630669007,-0.8008133751

B3PW91/6-31+G**

E(RB3PW91) = -536.031089581

Zero-point correction= 0.150712 (Hartree/Particle)
Thermal correction to Energy= 0.160269
Thermal correction to Enthalpy= 0.161213
Thermal correction to Gibbs Free Energy= 0.116434
Sum of electronic and ZPE= -535.880378
Sum of electronic and thermal Energies= -535.870821
Sum of electronic and thermal Enthalpies= -535.869876
Sum of electronic and thermal Free Energies= -535.914656

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	100.570	37.497	94.246

C,0,0.0375339902,0.0135389322,-0.0233727881
C,0,-0.0124797762,-0.0125325964,1.4679456603
C,0,1.271268197,-0.0261426104,1.9221607461
C,0,2.1990213571,-0.1690319143,0.8127546006
C,0,1.4842787608,-0.2575645763,-0.3606964765
C,0,0.1451477574,-2.6975525062,0.6906421693
H,0,-0.9226825305,0.103898934,2.0418499772
H,0,1.5801312636,0.0365456478,2.9599241798
H,0,3.2778636029,-0.1606557705,0.9073160423
C,0,0.8621426508,-2.4982352349,-0.4677504194
H,0,1.8781207066,-0.2184601728,-1.3684756524
H,0,0.4702474341,-2.441585117,-1.4754549413
H,0,-0.9338739727,-2.7147570131,0.7819040361
C,0,1.0707739817,-2.9450602264,1.7832909218
C,0,2.3553962752,-2.9156647124,1.3323065514
H,0,0.7599170232,-3.1058228241,2.809839749
H,0,3.2645018413,-3.0860640654,1.8943409367
C,0,2.3082593882,-2.8002300512,-0.1548601403
O,0,3.2135388606,-2.9756647107,-0.9477797988
O,0,-0.8662315712,0.2634389166,-0.7978323645

[3,3]-Sigmatropic rearrangement transition structure

G4
-0.2614576305D+01 EUMP2

Zero-point correction= 0.152158 (Hartree/Particle)
Thermal correction to Energy= 0.160731
Thermal correction to Enthalpy= 0.161675
Thermal correction to Gibbs Free Energy= 0.118534
Sum of electronic and ZPE= -536.101726
Sum of electronic and thermal Energies= -536.093153
Sum of electronic and thermal Enthalpies= -536.092209
Sum of electronic and thermal Free Energies= -536.135350

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	100.860	35.309	90.799

C,0,-0.4837124015,-0.0066875938,-1.8247741294
C,0,0.9887929723,-0.1147420761,-1.8105894471
C,0,1.3426432699,-1.1578293354,-0.9628934921
C,0,0.2696969606,-1.5094717171,-0.1456556716
C,0,-0.8911178546,-0.6523130614,-0.4848982482
C,0,0.2693665533,1.5095303529,0.1456426287
H,0,1.6259707762,0.376158244,-2.5338431431
H,0,2.3324576842,-1.5919938903,-0.8937361549
H,0,0.2299236621,-2.3579713821,0.5218956871
C,0,-0.8912394291,0.6521117881,0.484943307
H,0,-1.8741824327,-1.1165083443,-0.4357922241
H,0,-1.8744102411,1.1160873665,0.4358871659
H,0,0.2293692854,2.3580220878,-0.5219055251
C,0,1.3424327461,1.1581275492,0.9628262693
C,0,0.9888585898,0.1149594506,1.8105385337
H,0,2.3321465466,1.5925136068,0.8936194944
C,0,-0.4836219951,0.0065763819,1.8247982147
H,0,1.6261828745,-0.3757993626,2.5337593367
O,0,-1.2115970079,-0.5080327912,2.638488889
O,0,-1.2118435591,0.5077577266,-2.6384284908

M06/6-31G*
E(RM06) = -535.862630925

Zero-point correction= 0.152497 (Hartree/Particle)
Thermal correction to Energy= 0.161107

Thermal correction to Enthalpy= 0.162051
Thermal correction to Gibbs Free Energy= 0.118846
Sum of electronic and ZPE= -535.710134
Sum of electronic and thermal Energies= -535.701524
Sum of electronic and thermal Enthalpies= -535.700580
Sum of electronic and thermal Free Energies= -535.743785

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	101.096	35.357	90.932

C,0,-0.4777097302,0.002566331,-1.7980765529
C,0,0.9874064657,-0.1170001183,-1.7897351614
C,0,1.3392084657,-1.1574544374,-0.9422029632
C,0,0.2643776089,-1.5043668714,-0.128690789
C,0,-0.8875875102,-0.6503857182,-0.4765630963
C,0,0.2640471013,1.5044244029,0.1286785284
H,0,1.6279998562,0.3781804042,-2.5131824787
H,0,2.3333734595,-1.5898765689,-0.8627043422
H,0,0.2228588073,-2.3447020147,0.5568654454
C,0,-0.8877093022,0.6501852686,0.4766086378
H,0,-1.8768070983,-1.1123082569,-0.4272194427
H,0,-1.8770346827,1.1118865131,0.427315324
H,0,0.2223060052,2.3447493863,-0.5568767203
C,0,1.338997072,1.1577511049,0.942134857
C,0,0.9874707743,0.1172176095,1.7896845881
H,0,2.3330617369,1.590394531,0.8625852724
C,0,-0.4776183514,-0.0026755758,1.7981011459
H,0,1.6282120205,-0.3778197417,2.5130989844
O,0,-1.2042394559,-0.564172215,2.5865733351
O,0,-1.2044962429,0.5639009666,-2.5865115719

M06/6-31G**
E(RM06) = -535.874105447

Zero-point correction= 0.152300 (Hartree/Particle)
Thermal correction to Energy= 0.160916
Thermal correction to Enthalpy= 0.161861
Thermal correction to Gibbs Free Energy= 0.118657
Sum of electronic and ZPE= -535.721805
Sum of electronic and thermal Energies= -535.713189
Sum of electronic and thermal Enthalpies= -535.712245
Sum of electronic and thermal Free Energies= -535.755449

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 100.977 35.433 90.930

C,0,-0.4783675097,0.0018099669,-1.7984138105
C,0,0.9870669461,-0.116889675,-1.7908489867
C,0,1.3392669042,-1.1564204425,-0.9429298839
C,0,0.264761461,-1.5041749826,-0.1294092927
C,0,-0.8874156149,-0.6508496618,-0.4766175933
C,0,0.2644310133,1.5042326244,0.1293970497
H,0,1.6269945699,0.3791204596,-2.5122853193
H,0,2.3323678455,-1.5878330958,-0.8633837477
H,0,0.2249872441,-2.3422484629,0.5569586598
C,0,-0.8875375283,0.6506492519,0.4766631006
H,0,-1.8753222224,-1.1126314444,-0.4260281842
H,0,-1.8755499929,1.112209968,0.4261239641
H,0,0.2244350403,2.3422963803,-0.5569699609
C,0,1.3390557554,1.1567171253,0.9428617718
C,0,0.9871313365,0.1171071072,1.7907984303
H,0,2.332056559,1.588350914,0.8632647268
C,0,-0.4782762775,-0.0019193898,1.798438401
H,0,1.6272068348,-0.3787600597,2.512201903
O,0,-1.2054594553,-0.5625649209,2.5868024359
O,0,-1.2057159094,0.5622933378,-2.5867406638

M06/6-31+G*
E(RM06) = -535.883007768

Zero-point correction= 0.152162 (Hartree/Particle)
Thermal correction to Energy= 0.160802
Thermal correction to Enthalpy= 0.161746
Thermal correction to Gibbs Free Energy= 0.118460
Sum of electronic and ZPE= -535.730846
Sum of electronic and thermal Energies= -535.722206
Sum of electronic and thermal Enthalpies= -535.721262
Sum of electronic and thermal Free Energies= -535.764548

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 100.905 35.419 91.103

C,0,-0.470440711,0.0059987428,-1.8002999427
C,0,0.9907407373,-0.1315058111,-1.8056290784
C,0,1.3377039366,-1.1697526135,-0.9508343824

C,0,0.2587552638,-1.5102431007,-0.1380264462
C,0,-0.887659404,-0.6459921222,-0.4827470511
C,0,0.2584236127,1.5102994456,0.1380146847
H,0,1.6318669462,0.3592001907,-2.5322805798
H,0,2.3286719408,-1.6104211156,-0.87181116
H,0,0.2152391031,-2.3465880226,0.5532687983
C,0,-0.887780214,0.6457918137,0.4827927305
H,0,-1.8796469666,-1.1035439238,-0.4428329961
H,0,-1.8798722479,1.1031213144,0.4429287703
H,0,0.2146859332,2.34663367,-0.5532795727
C,0,1.3374899406,1.1700487516,0.9507661951
C,0,0.9908022961,0.131724036,1.8055783225
H,0,2.3283560058,1.6109373112,0.8716918135
C,0,-0.4703488103,-0.0061059889,1.8003244398
H,0,1.6320756142,-0.3588388848,2.5321966125
O,0,-1.1963434652,-0.5755429623,2.5887428552
O,0,-1.1966025113,0.5752742693,-2.5886810132

M06/6-31+G**

E(RM06) = -535.894479218

Zero-point correction= 0.151970 (Hartree/Particle)
Thermal correction to Energy= 0.160623
Thermal correction to Enthalpy= 0.161567
Thermal correction to Gibbs Free Energy= 0.118266
Sum of electronic and ZPE= -535.742509
Sum of electronic and thermal Energies= -535.733856
Sum of electronic and thermal Enthalpies= -535.732912
Sum of electronic and thermal Free Energies= -535.776213

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	100.792	35.509	91.135

C,0,-0.4708303309,0.0053754793,-1.8009433406
C,0,0.9905543007,-0.1322362909,-1.8078333614
C,0,1.3376966881,-1.1696439598,-0.9525531273
C,0,0.259117002,-1.510326367,-0.1392364029
C,0,-0.8872323316,-0.646165718,-0.4830078828
C,0,0.2587853506,1.5103828286,0.1392246597
H,0,1.6305314237,0.3584557434,-2.5332689299
H,0,2.3272633065,-1.6096912386,-0.8737136638
H,0,0.217131266,-2.3444487659,0.5526222315
C,0,-0.8873532107,0.6459655114,0.4830534997

H,0,-1.8780069358,-1.1033607366,-0.4424769405
H,0,-1.878232279,1.1029384116,0.4425725438
H,0,0.2165785933,2.3444950769,-0.5526328115
C,0,1.3374827663,1.1699401047,0.9524849584
C,0,0.9906157855,0.1324543813,1.8077825124
H,0,2.3269475063,1.610207322,0.8735944882
C,0,-0.4707385725,-0.0054828324,1.8009677966
H,0,1.6307398262,-0.3580950096,2.5331849179
O,0,-1.197337184,-0.5743292091,2.5890341072
O,0,-1.1975959706,0.574060269,-2.5889722549

M062X/6-31G*

E(RM062X) = -535.992236174

Zero-point correction= 0.154971 (Hartree/Particle)
Thermal correction to Energy= 0.163306
Thermal correction to Enthalpy= 0.164250
Thermal correction to Gibbs Free Energy= 0.121618
Sum of electronic and ZPE= -535.837265
Sum of electronic and thermal Energies= -535.828930
Sum of electronic and thermal Enthalpies= -535.827986
Sum of electronic and thermal Free Energies= -535.870619

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	102.476	34.465	89.727

C,0,-0.5132923013,-0.0362073359,-1.7926568751
C,0,0.9695027001,-0.037219338,-1.7351672606
C,0,1.354209311,-1.1020032337,-0.9312421295
C,0,0.3030145803,-1.4758002915,-0.0931264415
C,0,-0.8942901283,-0.6682149086,-0.4513106733
C,0,0.3026902479,1.4758646075,0.0931106124
H,0,1.5870479823,0.4874207837,-2.4540116818
H,0,2.3607168312,-1.49926017,-0.8604033572
H,0,0.2785158809,-2.350602004,0.5447682014
C,0,-0.8944159817,0.6680124145,0.4513563902
H,0,-1.8646276444,-1.1568957585,-0.3767223038
H,0,-1.8648662661,1.1564768265,0.3768172176
H,0,0.2779637542,2.3506602995,-0.5447834813
C,0,1.354011143,1.1023026983,0.9311729412
C,0,0.9695829747,0.03743377,1.7351186118
H,0,2.3604263808,1.4997841554,0.8602826098
C,0,-0.5132089125,0.0360909246,1.7926836711

H,0,1.5872818311,-0.4870678674,2.4539321414
O,0,-1.2519573907,-0.4348606576,2.6199069278
O,0,-1.2521879927,0.4345800853,-2.6198421204

B3LYP/6-31G*

E(RB3LYP) = -536.216011161

Zero-point correction= 0.152846 (Hartree/Particle)
Thermal correction to Energy= 0.161433
Thermal correction to Enthalpy= 0.162377
Thermal correction to Gibbs Free Energy= 0.119177
Sum of electronic and ZPE= -536.063165
Sum of electronic and thermal Energies= -536.054578
Sum of electronic and thermal Enthalpies= -536.053634
Sum of electronic and thermal Free Energies= -536.096834

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	101.301	35.245	90.923

C,0,-0.479478,-0.004336,-1.82798
C,0,0.991138,-0.127758,-1.823124
C,0,1.342383,-1.169058,-0.966996
C,0,0.265469,-1.514863,-0.148761
C,0,-0.892326,-0.649107,-0.488563
C,0,0.265051,1.51508,0.148899
H,0,1.631837,0.357032,-2.550238
H,0,2.332215,-1.608216,-0.896678
H,0,0.223977,-2.361295,0.524848
C,0,-0.892514,0.649001,0.488651
H,0,-1.877353,-1.114529,-0.447348
H,0,-1.877675,1.11414,0.447484
H,0,0.223377,2.36151,-0.524703
C,0,1.342113,1.169364,0.966918
C,0,0.991162,0.12785,1.822954
H,0,2.331855,1.608719,0.896558
C,0,-0.479437,0.004205,1.827988
H,0,1.632025,-0.356903,2.549948
O,0,-1.208742,-0.534689,2.636763
O,0,-1.20896,0.534348,-2.636737

B3PW91/6-31G*

E(RB3PW91) = -536.018033509

Zero-point correction= 0.153567 (Hartree/Particle)
Thermal correction to Energy= 0.162073
Thermal correction to Enthalpy= 0.163017
Thermal correction to Gibbs Free Energy= 0.120011
Sum of electronic and ZPE= -535.864466
Sum of electronic and thermal Energies= -535.855960
Sum of electronic and thermal Enthalpies= -535.855016
Sum of electronic and thermal Free Energies= -535.898023

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	101.702	34.990	90.515

C,0,-0.4907568394,-0.0145153923,-1.809120436
C,0,0.9827397538,-0.0849553455,-1.7768255388
C,0,1.3467404268,-1.1373361352,-0.9421465513
C,0,0.2775509442,-1.4965391116,-0.122204416
C,0,-0.892922176,-0.6540577064,-0.4714867409
C,0,0.2772273565,1.4965878565,0.1221810017
H,0,1.6176372897,0.4170372619,-2.4981295105
H,0,2.3433244189,-1.5617551798,-0.8729658225
H,0,0.2396418623,-2.3579122128,0.5339601016
C,0,-0.8930408463,0.6538485457,0.4715295078
H,0,-1.8719934413,-1.1313721903,-0.4190336194
H,0,-1.8722203902,1.1309463082,0.4191249338
H,0,0.2390923442,2.3579493815,-0.5339855185
C,0,1.3465373307,1.1376329843,0.9420770727
C,0,0.9828134941,0.0851817381,1.7767853926
H,0,2.3430222992,1.5622760716,0.8728444461
C,0,-0.4906654826,0.0144059626,1.809147588
H,0,1.6178583024,-0.4166601127,2.4980645805
O,0,-1.2231125391,-0.490240474,2.6326162466
O,0,-1.2233571079,0.48997275,-2.6325497176

B3PW91/6-31G**
E(RB3PW91) = -536.029808564

Zero-point correction= 0.153295 (Hartree/Particle)
Thermal correction to Energy= 0.161809
Thermal correction to Enthalpy= 0.162753
Thermal correction to Gibbs Free Energy= 0.119739
Sum of electronic and ZPE= -535.876513
Sum of electronic and thermal Energies= -535.867999
Sum of electronic and thermal Enthalpies= -535.867055

Sum of electronic and thermal Free Energies= -535.910069

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	101.537	35.062	90.531

C,0,-0.4906565709,-0.0145150367,-1.8095233203
C,0,0.9828791263,-0.0857752958,-1.7781869049
C,0,1.346440343,-1.1372736709,-0.94274246
C,0,0.2771104764,-1.4966574867,-0.1232295087
C,0,-0.8929187135,-0.6540660563,-0.4719947156
C,0,0.276785947,1.4967084135,0.1232081582
H,0,1.6180565128,0.4163862694,-2.4980919507
H,0,2.3421392767,-1.5619129413,-0.8733366162
H,0,0.2402411808,-2.3563536555,0.5340923117
C,0,-0.8930380661,0.6538583787,0.4720380051
H,0,-1.8713627534,-1.1312784888,-0.4191832039
H,0,-1.8715905748,1.1308538239,0.419275245
H,0,0.2396910847,2.3563938359,-0.5341149295
C,0,1.3462365762,1.1375708557,0.9426733208
C,0,0.982952185,0.0859998139,1.7781447518
H,0,2.3418365474,1.5624337054,0.8732159468
C,0,-0.4905657905,0.0144049814,1.809549972
H,0,1.6182771173,-0.4160127503,2.498023465
O,0,-1.2230762906,-0.4905414052,2.6327039383
O,0,-1.2233206138,0.4902717097,-2.632638505

B3PW91/6-31+G*

E(RB3PW91) = -536.036735338

Zero-point correction= 0.153266 (Hartree/Particle)
Thermal correction to Energy= 0.161793
Thermal correction to Enthalpy= 0.162737
Thermal correction to Gibbs Free Energy= 0.119683
Sum of electronic and ZPE= -535.883470
Sum of electronic and thermal Energies= -535.874942
Sum of electronic and thermal Enthalpies= -535.873998
Sum of electronic and thermal Free Energies= -535.917052

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	101.527	35.054	90.614

C,0,-0.484979761,-0.0114035043,-1.8098121572

C,0,0.9857251321,-0.0945768096,-1.7876023403
C,0,1.346159168,-1.1449153281,-0.9465366595
C,0,0.2728539449,-1.5008119416,-0.1288726012
C,0,-0.8935912694,-0.6509561489,-0.4764011864
C,0,0.2725264133,1.5008670594,0.1288560267
H,0,1.6210449326,0.4045872323,-2.5110346428
H,0,2.3407040152,-1.5747943807,-0.8767753836
H,0,0.2335687344,-2.3583927499,0.5330403217
C,0,-0.8937114631,0.6507516155,0.476445723
H,0,-1.87503394,-1.1246602284,-0.4314370539
H,0,-1.8752619101,1.1242370703,0.43153105
H,0,0.2330159758,2.3584379507,-0.5330562862
C,0,1.3459521218,1.1452132969,0.946468136
C,0,0.9857952301,0.0947975921,1.7875555406
H,0,2.3403971365,1.5753150039,0.8766560504
C,0,-0.4848898113,0.0112933778,1.8098374734
H,0,1.6212627426,-0.4042215562,2.5109580747
O,0,-1.2175876187,-0.4983456212,2.6342687063
O,0,-1.2178327738,0.4980730701,-2.6342057918

B3PW91/6-31+G**

E(RB3PW91) = -536.048425953

Zero-point correction= 0.152995 (Hartree/Particle)
Thermal correction to Energy= 0.161535
Thermal correction to Enthalpy= 0.162479
Thermal correction to Gibbs Free Energy= 0.119408
Sum of electronic and ZPE= -535.895431
Sum of electronic and thermal Energies= -535.886891
Sum of electronic and thermal Enthalpies= -535.885947
Sum of electronic and thermal Free Energies= -535.929018

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	101.365	35.137	90.650

C,0,-0.4846363528,-0.0112870577,-1.8104529924
C,0,0.9860371018,-0.0960396684,-1.7898065437
C,0,1.3458435258,-1.1455146452,-0.9478190897
C,0,0.2723579119,-1.501177004,-0.130285369
C,0,-0.8934274614,-0.6507604204,-0.477112415
C,0,0.2720305994,1.5012313408,0.1302681855
H,0,1.6212359959,0.4025963879,-2.5125223048
H,0,2.3392737818,-1.5758130969,-0.8778757784

H,0,0.2338542919,-2.3571674756,0.5325132891
C,0,-0.8935474435,0.6505554695,0.4771567736
H,0,-1.8743322651,-1.1241721493,-0.4323450994
H,0,-1.8745599437,1.1237486941,0.4324387241
H,0,0.2333020435,2.3572119842,-0.5325300221
C,0,1.3456365713,1.145812399,0.9477505414
C,0,0.9861070919,0.0962610721,1.7897602751
H,0,2.3389668408,1.5763333725,0.8777564061
C,0,-0.4845462179,0.011177216,1.8104784437
H,0,1.6214534587,-0.4022296458,2.5124466594
O,0,-1.2173435863,-0.498939704,2.6344548926
O,0,-1.2175889439,0.4986679312,-2.6343915763

Cyclopentandienone Structure

G4
-0.1266419612D+01 EUMP2

Zero-point correction= 0.074155 (Hartree/Particle)
Thermal correction to Energy= 0.078849
Thermal correction to Enthalpy= 0.079793
Thermal correction to Gibbs Free Energy= 0.046305
Sum of electronic and ZPE= -268.048505
Sum of electronic and thermal Energies= -268.043811
Sum of electronic and thermal Enthalpies= -268.042866
Sum of electronic and thermal Free Energies= -268.076354

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	49.479	17.375	70.481

C,0,-0.0256282009,0.0000046077,0.020417645
C,0,0.0110245103,-0.0001870032,1.5310970919
H,0,0.9267886318,-0.0002449083,2.1031955847
C,0,-1.2542609835,-0.0003098382,1.9611506404
H,0,-1.5946115927,-0.0004920514,2.9887838468
C,0,-1.4902890264,0.000124381,-0.3514185464
H,0,-1.8443073824,0.000329621,-1.3715124338
C,0,-2.1910696133,-0.0001175623,0.7864744044
H,0,-3.2686691805,-0.0001474047,0.8896627359
O,0,0.9179948377,0.0002611583,-0.7321239688

M06/6-31G*
E(RM06) = -267.919536239

Zero-point correction= 0.074322 (Hartree/Particle)
Thermal correction to Energy= 0.079043
Thermal correction to Enthalpy= 0.079987
Thermal correction to Gibbs Free Energy= 0.046455
Sum of electronic and ZPE= -267.845214
Sum of electronic and thermal Energies= -267.840493
Sum of electronic and thermal Enthalpies= -267.839549
Sum of electronic and thermal Free Energies= -267.873081

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	49.600	17.439	70.573

C,0,-0.0307030666,0.0000703636,0.0244655808
C,0,0.0094738758,-0.0001934933,1.5274519356
H,0,0.9290512412,-0.0002732495,2.1004944009
C,0,-1.2552833593,-0.0003032561,1.9579718628
H,0,-1.5941380359,-0.000492352,2.9900405088
C,0,-1.4870804304,0.0001156478,-0.3490952112
H,0,-1.8411687191,0.0002978211,-1.3731174816
C,0,-2.1881983882,-0.0001078336,0.7881785417
H,0,-3.2697893416,-0.0001423878,0.8889223831
O,0,0.9148098244,0.0002497395,-0.7295847681

M06/6-31G**
E(RM06) = -267.925532865

Zero-point correction= 0.074271 (Hartree/Particle)
Thermal correction to Energy= 0.078992
Thermal correction to Enthalpy= 0.079936
Thermal correction to Gibbs Free Energy= 0.046404
Sum of electronic and ZPE= -267.851262
Sum of electronic and thermal Energies= -267.846541
Sum of electronic and thermal Enthalpies= -267.845597
Sum of electronic and thermal Free Energies= -267.879129

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	49.568	17.447	70.576

C,0,-0.0308146714,0.000063571,0.0245545848
C,0,0.0094917539,-0.0001930482,1.52759851
H,0,0.927394704,-0.0002711977,2.1008469852

C,0,-1.255142503,-0.0003040813,1.9577615919
H,0,-1.5932747142,-0.0004915482,2.9886806481
C,0,-1.4872193485,0.0001161175,-0.3491452555
H,0,-1.841881002,0.0002997028,-1.3715809132
C,0,-2.1879620518,-0.0001086946,0.7880879915
H,0,-3.2682714873,-0.0001417447,0.8883832585
O,0,0.9146529264,0.0002519233,-0.7294596413

M06/6-31+G*
E(RM06) = -267.930369444

Zero-point correction= 0.074141 (Hartree/Particle)
Thermal correction to Energy= 0.078873
Thermal correction to Enthalpy= 0.079817
Thermal correction to Gibbs Free Energy= 0.046264
Sum of electronic and ZPE= -267.856228
Sum of electronic and thermal Energies= -267.851496
Sum of electronic and thermal Enthalpies= -267.850552
Sum of electronic and thermal Free Energies= -267.884106

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	49.494	17.484	70.619

C,0,-0.0318281124,0.0000281064,0.0253628335
C,0,0.0103054369,-0.0001904198,1.5275480436
H,0,0.9310612526,-0.0002491639,2.0996006125
C,0,-1.2561849603,-0.0003125324,1.9590355491
H,0,-1.5935535968,-0.0004914299,2.9919401921
C,0,-1.4869890698,0.0001185611,-0.3499272184
H,0,-1.8398501553,0.0003216334,-1.3748781628
C,0,-2.1894359844,-0.0001164446,0.7888210261
H,0,-3.271511342,-0.0001403526,0.8879296892
O,0,0.9149601405,0.0002530421,-0.7297048013

M06/6-31+G**
E(RM06) = -267.936390105

Zero-point correction= 0.074086 (Hartree/Particle)
Thermal correction to Energy= 0.078821
Thermal correction to Enthalpy= 0.079766
Thermal correction to Gibbs Free Energy= 0.046206
Sum of electronic and ZPE= -267.862304
Sum of electronic and thermal Energies= -267.857569

Sum of electronic and thermal Enthalpies= -267.856625
Sum of electronic and thermal Free Energies= -267.890184

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	49.461	17.507	70.632

C,0,-0.0319887409,0.000018701,0.0254909253
C,0,0.0102960951,-0.0001901396,1.5277369818
H,0,0.9293541675,-0.0002462728,2.0996685608
C,0,-1.2561263203,-0.000313632,1.9589283642
H,0,-1.5926147591,-0.000490222,2.9904972264
C,0,-1.4871753402,0.0001188927,-0.3499601462
H,0,-1.840296176,0.0003243324,-1.373228978
C,0,-2.1893184398,-0.0001176283,0.788787692
H,0,-3.2698956615,-0.0001393712,0.8873354266
O,0,0.9147387685,0.0002563397,-0.729528309

M062X/6-31G*
E(RM062X) = -267.986701691

Zero-point correction= 0.075416 (Hartree/Particle)
Thermal correction to Energy= 0.080080
Thermal correction to Enthalpy= 0.081025
Thermal correction to Gibbs Free Energy= 0.047571
Sum of electronic and ZPE= -267.911286
Sum of electronic and thermal Energies= -267.906621
Sum of electronic and thermal Enthalpies= -267.905677
Sum of electronic and thermal Free Energies= -267.939131

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	50.251	17.147	70.410

C,0,-0.0281516685,0.0000819838,0.0224308426
C,0,0.0117079491,-0.0002014751,1.5322794586
H,0,0.9286446803,-0.0002979932,2.1050783745
C,0,-1.2527926455,-0.0002887304,1.9602829211
H,0,-1.5915568709,-0.0004859049,2.9895081808
C,0,-1.4912898251,0.0001112037,-0.3523471069
H,0,-1.8457283911,0.0002799923,-1.3737406896
C,0,-2.1898972916,-0.0000988916,0.7852364191
H,0,-3.2686960482,-0.000144016,0.8865236957
O,0,0.9147337119,0.0002648312,-0.7295243433

B3LYP/6-31G*

E(RB3LYP) = -268.103659786

Zero-point correction= 0.074417 (Hartree/Particle)
Thermal correction to Energy= 0.079117
Thermal correction to Enthalpy= 0.080061
Thermal correction to Gibbs Free Energy= 0.046559
Sum of electronic and ZPE= -268.029243
Sum of electronic and thermal Energies= -268.024543
Sum of electronic and thermal Enthalpies= -268.023599
Sum of electronic and thermal Free Energies= -268.057101

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	49.647	17.378	70.512

C,0,-0.0262292364,-0.0004814595,0.0208966297
C,0,0.0125343463,-0.0001399138,1.5310803006
H,0,0.9301653483,0.0000278414,2.1042952282
C,0,-1.2560675845,-0.0004160881,1.9632047198
H,0,-1.5954294,-0.0004817679,2.9932794009
C,0,-1.4899382731,0.0001703793,-0.3528874578
H,0,-1.8446260146,0.0005946133,-1.3750504708
C,0,-2.1934761633,-0.0002155705,0.7877767313
H,0,-3.2732361849,-0.0001252511,0.889465209
O,0,0.9232760029,0.0002884935,-0.7363338348

B3PW91/6-31G*

E(RB3PW91) = -267.999261573

Zero-point correction= 0.074618 (Hartree/Particle)
Thermal correction to Energy= 0.079324
Thermal correction to Enthalpy= 0.080268
Thermal correction to Gibbs Free Energy= 0.046754
Sum of electronic and ZPE= -267.924644
Sum of electronic and thermal Energies= -267.919938
Sum of electronic and thermal Enthalpies= -267.918994
Sum of electronic and thermal Free Energies= -267.952507

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	49.776	17.368	70.535

C,0,-0.0286388067,-0.0001721285,0.0228183126
C,0,0.0119150533,-0.0001591266,1.5291850734
H,0,0.9290709881,-0.0001124024,2.1036504769
C,0,-1.2561254782,-0.000363481,1.9602166366
H,0,-1.5948582901,-0.0004961207,2.9909352105
C,0,-1.4882277532,0.00015134,-0.3518617528
H,0,-1.8442425965,0.0004579897,-1.3738391777
C,0,-2.1905748873,-0.0001672141,0.7884989029
H,0,-3.270822872,-0.0001449912,0.8894275138
O,0,0.9194774834,0.0002274112,-0.7333047401

B3PW91/6-31G**
E(RB3PW91) = -268.005438843

Zero-point correction= 0.074523 (Hartree/Particle)
Thermal correction to Energy= 0.079231
Thermal correction to Enthalpy= 0.080175
Thermal correction to Gibbs Free Energy= 0.046660
Sum of electronic and ZPE= -267.930915
Sum of electronic and thermal Energies= -267.926208
Sum of electronic and thermal Enthalpies= -267.925264
Sum of electronic and thermal Free Energies= -267.958779

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	49.718	17.383	70.538

C,0,-0.0286670458,-0.0001286678,0.0228407851
C,0,0.0120147401,-0.0001627138,1.5292376463
H,0,0.9277647881,-0.0001349279,2.1046205097
C,0,-1.2559667823,-0.0003552428,1.959911066
H,0,-1.593717092,-0.0004974537,2.9902511641
C,0,-1.48825666,0.0001477574,-0.3519705542
H,0,-1.8454793714,0.000435851,-1.3727812093
C,0,-2.1902414225,-0.0001593176,0.7884123861
H,0,-3.2699018743,-0.0001467568,0.888466487
O,0,0.9194235608,0.0002227485,-0.7332618246

B3PW91/6-31+G*
E(RB3PW91) = -268.009366742

Zero-point correction= 0.074440 (Hartree/Particle)
Thermal correction to Energy= 0.079156
Thermal correction to Enthalpy= 0.080100

Thermal correction to Gibbs Free Energy= 0.046567
Sum of electronic and ZPE= -267.934927
Sum of electronic and thermal Energies= -267.930211
Sum of electronic and thermal Enthalpies= -267.929267
Sum of electronic and thermal Free Energies= -267.962799

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	49.671	17.413	70.575

C,0,-0.0297573814,-0.0002056528,0.0237103737
C,0,0.012743075,-0.0001596194,1.5292876404
H,0,0.9309092493,-0.0001043294,2.1028435137
C,0,-1.256885318,-0.0003671417,1.9612830411
H,0,-1.5942418497,-0.0004922712,2.9927470501
C,0,-1.4881435889,0.000150867,-0.3526919245
H,0,-1.8430465975,0.0004655752,-1.3754520359
C,0,-2.1917837165,-0.000170196,0.7890023043
H,0,-3.2724521935,-0.0001398965,0.888423774
O,0,0.9196311619,0.0002439413,-0.7334272805

B3PW91/6-31+G**
E(RB3PW91) = -268.015532936

Zero-point correction= 0.074338 (Hartree/Particle)
Thermal correction to Energy= 0.079058
Thermal correction to Enthalpy= 0.080002
Thermal correction to Gibbs Free Energy= 0.046464
Sum of electronic and ZPE= -267.941195
Sum of electronic and thermal Energies= -267.936475
Sum of electronic and thermal Enthalpies= -267.935531
Sum of electronic and thermal Free Energies= -267.969069

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	49.609	17.440	70.586

C,0,-0.0298478288,-0.0001682586,0.0237824279
C,0,0.0128104367,-0.0001626192,1.5293991659
H,0,0.9296914547,-0.0001231399,2.1034527758
C,0,-1.2568084421,-0.0003601754,1.9611075212
H,0,-1.5931140466,-0.0004935169,2.9920480056
C,0,-1.4882371842,0.0001479238,-0.3527823278
H,0,-1.8439118788,0.0004471129,-1.3744000012

C,0,-2.1915952902,-0.0001636132,0.7889665616
H,0,-3.2715196018,-0.0001416291,0.8874792493
O,0,0.9195052219,0.000239192,-0.7333269221

Dicyclopentadienone

G4
-0.2571749505D+01 EUMP2

Zero-point correction= 0.154967 (Hartree/Particle)
Thermal correction to Energy= 0.163576
Thermal correction to Enthalpy= 0.164520
Thermal correction to Gibbs Free Energy= 0.121081
Sum of electronic and ZPE= -536.141942
Sum of electronic and thermal Energies= -536.133333
Sum of electronic and thermal Enthalpies= -536.132389
Sum of electronic and thermal Free Energies= -536.175828

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	102.645	35.204	91.425

C,0,0.0011008245,-0.0026611997,0.0018229536
C,0,0.0010011765,-0.0010182386,1.5135740108
C,0,2.1929241394,-0.0020841154,0.7671208448
C,0,1.2735364056,-0.002339928,-0.4300619115
H,0,-0.8955432399,-0.0105551832,-0.6033030007
H,0,1.612119707,-0.0098678498,-1.4577679173
C,0,0.5716007474,-1.3659820855,2.0291393727
H,0,0.4772000815,-1.4234487393,3.1168758537
C,0,2.0535359481,-1.3696662532,1.5428481408
H,0,2.7745735503,-1.3721427524,2.3673667377
H,0,-0.9009822499,0.3391771456,2.0156350287
H,0,3.2139411828,0.3441906867,0.621325088
C,0,1.2891409923,0.847005633,1.7087832118
O,0,1.5181619209,1.8108521445,2.3698927781
C,0,-0.0615109408,-2.6153275119,1.3926496313
O,0,-1.216928485,-2.9538403188,1.497600653
C,0,2.1638683362,-2.62452131,0.720545673
C,0,1.013414808,-3.3047435658,0.6386378952
H,0,0.8404882097,-4.2305293483,0.104407204
H,0,3.0966818854,-2.91708621,0.2490497524

M06/6-31G*

E(RM06) = -535.912261171

Zero-point correction= 0.155427 (Hartree/Particle)
Thermal correction to Energy= 0.164078
Thermal correction to Enthalpy= 0.165022
Thermal correction to Gibbs Free Energy= 0.121447
Sum of electronic and ZPE= -535.756834
Sum of electronic and thermal Energies= -535.748183
Sum of electronic and thermal Enthalpies= -535.747239
Sum of electronic and thermal Free Energies= -535.790814

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	102.961	35.178	91.712

C,0,-0.0048515202,-0.0228708987,0.0191452875
C,0,0.009636558,-0.0075460877,1.5233513184
C,0,2.1835185949,-0.0093962333,0.767590477
C,0,1.2644350206,-0.0251075529,-0.4206658822
H,0,-0.90818105,-0.052064775,-0.583129311
H,0,1.5957155063,-0.0523317114,-1.4549240661
C,0,0.5821388648,-1.3625508039,2.0271476721
H,0,0.4861101126,-1.4360315394,3.1180455674
C,0,2.0545590181,-1.3626971552,1.546427891
H,0,2.7765467951,-1.3558010959,2.3758044661
H,0,-0.8912657075,0.3346230931,2.0353925099
H,0,3.2051540058,0.3468403782,0.6172357327
C,0,1.288231526,0.8320800804,1.7014572946
O,0,1.5248345727,1.7972029002,2.3666849723
C,0,-0.0547976092,-2.5837947785,1.3699495383
O,0,-1.2276925907,-2.8802292444,1.4289105128
C,0,2.1694244809,-2.6131992757,0.7306629957
C,0,1.0169607463,-3.2889913119,0.6385790309
H,0,0.8405879749,-4.2131931603,0.0956611544
H,0,3.1072597005,-2.9095338277,0.2628128381

M06/6-31G**
E(RM06) = -535.923230406

Zero-point correction= 0.155178 (Hartree/Particle)
Thermal correction to Energy= 0.163842
Thermal correction to Enthalpy= 0.164786
Thermal correction to Gibbs Free Energy= 0.121196
Sum of electronic and ZPE= -535.768052

Sum of electronic and thermal Energies= -535.759389
Sum of electronic and thermal Enthalpies= -535.758444
Sum of electronic and thermal Free Energies= -535.802034

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	102.812	35.265	91.742

C,0,-0.0047435944,-0.0232260588,0.0199606116
C,0,0.0097280356,-0.0071439725,1.5241121865
C,0,2.1836800516,-0.0092165789,0.7679814756
C,0,1.2643379083,-0.0255868947,-0.4199884627
H,0,-0.9066251127,-0.0527417141,-0.5819638639
H,0,1.5943577514,-0.053526055,-1.4531542352
C,0,0.5822791356,-1.3624394009,2.0271456481
H,0,0.4861634083,-1.4378753812,3.1166566108
C,0,2.0542502544,-1.3627336406,1.5464213179
H,0,2.7758210387,-1.3568971609,2.3745591955
H,0,-0.8903810811,0.334197364,2.0354260532
H,0,3.2042554934,0.3461694045,0.6174850772
C,0,1.2882990441,0.8326622704,1.7012783314
O,0,1.5245452839,1.7988957596,2.3648986961
C,0,-0.054717223,-2.5830984864,1.3694681445
O,0,-1.2278767236,-2.8784218521,1.4272893918
C,0,2.1692829627,-2.6129620394,0.7303867767
C,0,1.0172855033,-3.2890851489,0.6386589218
H,0,0.8424746008,-4.2125330801,0.0965346358
H,0,3.1059082625,-2.9090303338,0.2629834871

M06/6-31+G*

E(RM06) = -535.931043586

Zero-point correction= 0.155139 (Hartree/Particle)
Thermal correction to Energy= 0.163787
Thermal correction to Enthalpy= 0.164731
Thermal correction to Gibbs Free Energy= 0.121179
Sum of electronic and ZPE= -535.775905
Sum of electronic and thermal Energies= -535.767256
Sum of electronic and thermal Enthalpies= -535.766312
Sum of electronic and thermal Free Energies= -535.809865

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	102.778	35.209	91.665

C,0,-0.0049181157,-0.0197203729,0.0141007212
C,0,0.0079042577,-0.0051604223,1.5189063774
C,0,2.1841070225,-0.0061673417,0.7661547455
C,0,1.266613005,-0.0205190787,-0.424486423
H,0,-0.9077331955,-0.0498260841,-0.5899181552
H,0,1.5984465547,-0.046695116,-1.4591592079
C,0,0.5804197998,-1.3613171672,2.0250544301
H,0,0.4830469328,-1.431585244,3.1164871215
C,0,2.0537498385,-1.3616419612,1.5437199766
H,0,2.7760363541,-1.3557693177,2.3731166431
H,0,-0.8921130933,0.3385923699,2.0316239021
H,0,3.2058309106,0.3518831676,0.6198130743
C,0,1.2878330215,0.8270496343,1.7015704067
O,0,1.5275088553,1.7841049529,2.3815490025
C,0,-0.0518554856,-2.5859352094,1.3745387495
O,0,-1.2258219578,-2.888561017,1.4403821267
C,0,2.1690002412,-2.6124879538,0.728762105
C,0,1.0161625425,-3.292649968,0.6424489198
H,0,0.8383795278,-4.2194007954,0.1037562065
H,0,3.1057279838,-2.9087860754,0.2577192776

M06/6-31+G**
E(RM06) = -535.941998176

Zero-point correction= 0.154902 (Hartree/Particle)
Thermal correction to Energy= 0.163565
Thermal correction to Enthalpy= 0.164509
Thermal correction to Gibbs Free Energy= 0.120939
Sum of electronic and ZPE= -535.787096
Sum of electronic and thermal Energies= -535.778434
Sum of electronic and thermal Enthalpies= -535.777489
Sum of electronic and thermal Free Energies= -535.821059

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	102.638	35.306	91.700

C,0,-0.004860108,-0.0198937715,0.0148633211
C,0,0.0080305825,-0.0046587498,1.5196889119
C,0,2.1843177287,-0.0058764462,0.7665334454
C,0,1.2665432294,-0.0208279638,-0.4238993272
H,0,-0.9060829369,-0.0504207017,-0.5887331618
H,0,1.5970231783,-0.0478558656,-1.4573192498

C,0,0.5805543639,-1.3612298375,2.0249343405
H,0,0.4825298189,-1.4338816628,3.1148442917
C,0,2.0535127017,-1.3616966542,1.5436476377
H,0,2.7753970489,-1.3569307684,2.3716371838
H,0,-0.8909751542,0.3385191291,2.031718399
H,0,3.2047916353,0.3516223843,0.6202135962
C,0,1.2879345751,0.8276649119,1.7013582902
O,0,1.5272739025,1.7858779281,2.3797055901
C,0,-0.051716945,-2.5853612486,1.3740227756
O,0,-1.2258800875,-2.8870832564,1.4388728177
C,0,2.1690028627,-2.612408948,0.7285428742
C,0,1.0165886031,-3.292958352,0.6426430507
H,0,0.8400397197,-4.2188185618,0.1049731232
H,0,3.1043002808,-2.9083745652,0.2578920898

M062X/6-31G*

E(RM062X) = -536.046475603

Zero-point correction= 0.157468 (Hartree/Particle)
Thermal correction to Energy= 0.165995
Thermal correction to Enthalpy= 0.166940
Thermal correction to Gibbs Free Energy= 0.123619
Sum of electronic and ZPE= -535.889008
Sum of electronic and thermal Energies= -535.880480
Sum of electronic and thermal Enthalpies= -535.879536
Sum of electronic and thermal Free Energies= -535.922857

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	104.164	34.674	91.176

C,0,-0.0048650727,-0.029198259,0.0169224722
C,0,0.004641169,0.0000689202,1.527228871
C,0,2.1892463399,-0.0048788561,0.7693982657
C,0,1.2637093864,-0.0334245272,-0.4212544028
H,0,-0.9043861977,-0.0720912841,-0.5854579256
H,0,1.5934704474,-0.0775380369,-1.4526106975
C,0,0.5786354616,-1.3579548038,2.0360840995
H,0,0.4829244931,-1.4333809097,3.1231492637
C,0,2.0566745462,-1.3602300788,1.5529518114
H,0,2.7755126471,-1.3594207889,2.3795177676
H,0,-0.893476188,0.3452962555,2.0345072513
H,0,3.2073612956,0.3489560192,0.6157933318
C,0,1.2907295198,0.8405981045,1.7065867139

O,0,1.52849025,1.8007390345,2.3742180695
C,0,-0.0576659127,-2.5813892705,1.371198242
O,0,-1.2248095713,-2.8866123048,1.4350563889
C,0,2.1695017719,-2.6126745046,0.7254508042
C,0,1.0175178228,-3.2843649425,0.6235811299
H,0,0.8389224733,-4.2013127058,0.0744191768
H,0,3.1061903183,-2.905780061,0.2593993665

B3LYP/6-31G*

E(RB3LYP) = -536.259619780

Zero-point correction= 0.155698 (Hartree/Particle)
Thermal correction to Energy= 0.164303
Thermal correction to Enthalpy= 0.165247
Thermal correction to Gibbs Free Energy= 0.121804
Sum of electronic and ZPE= -536.103922
Sum of electronic and thermal Energies= -536.095317
Sum of electronic and thermal Enthalpies= -536.094373
Sum of electronic and thermal Free Energies= -536.137816

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	103.102	35.102	91.433

C,0,-0.0000423574,-0.0002055121,0.0001065418
C,0,0.0000185332,-0.0001436123,1.5134465414
C,0,2.1942662058,-0.0000489969,0.7677068492
C,0,1.2756914909,0.0008372816,-0.4320263751
H,0,-0.8969724736,-0.0102950349,-0.6090355339
H,0,1.6134414158,-0.0072054752,-1.4626472832
C,0,0.571106868,-1.3664659508,2.0295951857
H,0,0.4780605616,-1.4227066721,3.1193291367
C,0,2.0553238477,-1.3699746572,1.5425218595
H,0,2.7760819635,-1.3736526691,2.3695514716
H,0,-0.9030417187,0.3416590206,2.0168788818
H,0,3.2164831096,0.3498497344,0.6238601248
C,0,1.2881275054,0.8471044611,1.7080671447
O,0,1.5182956076,1.8166346444,2.3750490116
C,0,-0.0605258761,-2.61779939,1.3950601465
O,0,-1.222982143,-2.9582031333,1.5018499953
C,0,2.1653687716,-2.6263814908,0.7188312153
C,0,1.0119834737,-3.3092456221,0.6392523723
H,0,0.8395317986,-4.2367868342,0.104198925
H,0,3.0981074721,-2.9215617514,0.244543896

B3PW91/6-31G*
E(RB3PW91) = -536.064663344

Zero-point correction= 0.156289 (Hartree/Particle)
Thermal correction to Energy= 0.164883
Thermal correction to Enthalpy= 0.165827
Thermal correction to Gibbs Free Energy= 0.122370
Sum of electronic and ZPE= -535.908374
Sum of electronic and thermal Energies= -535.899780
Sum of electronic and thermal Enthalpies= -535.898836
Sum of electronic and thermal Free Energies= -535.942294

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	103.466	34.949	91.464

C,0,0.0040186474,-0.0121589748,0.00634618
C,0,0.0037608994,-0.0054805868,1.5141331595
C,0,2.1928114825,-0.0046804232,0.7724562427
C,0,1.279663881,-0.0101148065,-0.4245396366
H,0,-0.8924123018,-0.0281712408,-0.6039537237
H,0,1.6179296581,-0.0232076669,-1.4552578619
C,0,0.5749200979,-1.3638777105,2.0296999151
H,0,0.4814776235,-1.4211337017,3.1197189334
C,0,2.0519899915,-1.3672394463,1.5445885567
H,0,2.7735380492,-1.3750148385,2.3714906187
H,0,-0.9000900021,0.3363726349,2.0165996487
H,0,3.2150802267,0.3462511726,0.6297391185
C,0,1.2858835998,0.8412850027,1.7032904121
O,0,1.512739822,1.8145815148,2.3633075142
C,0,-0.0587970105,-2.6083484135,1.394865977
O,0,-1.2194360038,-2.9473623328,1.5049894618
C,0,2.1608795861,-2.6147784869,0.7161410386
C,0,1.007357261,-3.2952993407,0.6325574805
H,0,0.8335069236,-4.2189675329,0.0907951604
H,0,3.0935016247,-2.9072464826,0.2391719114

B3PW91/6-31G**
E(RB3PW91) = -536.076039239

Zero-point correction= 0.155974 (Hartree/Particle)
Thermal correction to Energy= 0.164578
Thermal correction to Enthalpy= 0.165523

Thermal correction to Gibbs Free Energy= 0.122051
Sum of electronic and ZPE= -535.920066
Sum of electronic and thermal Energies= -535.911461
Sum of electronic and thermal Enthalpies= -535.910517
Sum of electronic and thermal Free Energies= -535.953988

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	103.274	35.033	91.493

C,0,0.00400908,-0.0122582839,0.0072054199
C,0,0.0038323472,-0.0051495923,1.5149210362
C,0,2.1929095235,-0.0046458596,0.7727941715
C,0,1.279435905,-0.0104140186,-0.4238564647
H,0,-0.8914225572,-0.0278132289,-0.6032327627
H,0,1.6164252295,-0.0232246492,-1.4541901036
C,0,0.5749622018,-1.3638693411,2.0295409234
H,0,0.4814810182,-1.4230418978,3.118815554
C,0,2.051656828,-1.3673569865,1.5445070439
H,0,2.7730834184,-1.3759120246,2.3706974993
H,0,-0.8996010875,0.3363419835,2.0169973557
H,0,3.2146279975,0.3456766989,0.6295472381
C,0,1.2859357818,0.841770046,1.7030252104
O,0,1.5124681199,1.8162372778,2.3613520041
C,0,-0.0586928172,-2.6079068375,1.3943546505
O,0,-1.2197281474,-2.9458703365,1.5031353535
C,0,2.1608840802,-2.6147830238,0.7162207871
C,0,1.0078213432,-3.2956733348,0.6329848374
H,0,0.8353903855,-4.2191023592,0.0916754907
H,0,3.0928454058,-2.907595892,0.2396448624

B3PW91/6-31+G*
E(RB3PW91) = -536.082252982

Zero-point correction= 0.156012 (Hartree/Particle)
Thermal correction to Energy= 0.164607
Thermal correction to Enthalpy= 0.165551
Thermal correction to Gibbs Free Energy= 0.122108
Sum of electronic and ZPE= -535.926241
Sum of electronic and thermal Energies= -535.917646
Sum of electronic and thermal Enthalpies= -535.916702
Sum of electronic and thermal Free Energies= -535.960145

	E	CV	S

KCal/Mol Cal/Mol-K Cal/Mol-K
Total 103.293 34.987 91.435

C,0,0.0040524999,-0.0087653991,0.0020501091
C,0,0.0023084425,-0.0038347174,1.5104434728
C,0,2.1932851696,-0.0023024424,0.7716676573
C,0,1.2817274322,-0.0057412074,-0.4276929463
H,0,-0.8919563469,-0.0246951306,-0.6097577562
H,0,1.6207862202,-0.0171690467,-1.4586855672
C,0,0.5734487886,-1.3632735016,2.0280035196
H,0,0.4789162545,-1.4176784727,3.1184240034
C,0,2.0511694046,-1.3667622633,1.5423870343
H,0,2.7728887395,-1.3756216975,2.3694584324
H,0,-0.9008833702,0.3392886816,2.0134216344
H,0,3.2156733584,0.3502136765,0.6325961344
C,0,1.2852756926,0.836936302,1.702827759
O,0,1.5141371282,1.8048723025,2.3737544399
C,0,-0.0560142229,-2.6101222326,1.398467703
O,0,-1.2167980683,-2.9551600164,1.5163466011
C,0,2.1603738147,-2.6145003829,0.7143633924
C,0,1.0066108476,-3.2988334592,0.6358561829
H,0,0.8312720702,-4.2246619653,0.0975733965
H,0,3.0920502011,-2.9067806878,0.2346349043

B3PW91/6-31+G**
E(RB3PW91) = -536.093526238

Zero-point correction= 0.155702 (Hartree/Particle)
Thermal correction to Energy= 0.164309
Thermal correction to Enthalpy= 0.165253
Thermal correction to Gibbs Free Energy= 0.121794
Sum of electronic and ZPE= -535.937824
Sum of electronic and thermal Energies= -535.929218
Sum of electronic and thermal Enthalpies= -535.928273
Sum of electronic and thermal Free Energies= -535.971733

E CV S
KCal/Mol Cal/Mol-K Cal/Mol-K
Total 103.105 35.080 91.468

C,0,0.0039559224,-0.0087191048,0.0028488543
C,0,0.0023919997,-0.0033707791,1.5112420539
C,0,2.1934237651,-0.0021533905,0.771932908
C,0,1.2814819127,-0.0059179301,-0.4271324075

H,0,-0.8909676835,-0.0243612027,-0.6089719151
H,0,1.6191740105,-0.017260095,-1.4576099527
C,0,0.5734723831,-1.363253449,2.0277461549
H,0,0.4783468707,-1.419942634,3.1173081902
C,0,2.0509058848,-1.3668505998,1.5422596177
H,0,2.772515493,-1.3765218553,2.3684719282
H,0,-0.9002065905,0.3395870144,2.013871339
H,0,3.215105459,0.3499747745,0.6324264108
C,0,1.2853917829,0.8373971455,1.7025481512
O,0,1.5140406989,1.8063687823,2.3719966844
C,0,-0.0558670052,-2.6096842107,1.3978220916
O,0,-1.2169764879,-2.9538689828,1.514503717
C,0,2.1605411398,-2.6146027012,0.7145087996
C,0,1.0072040807,-3.2993743689,0.6363738034
H,0,0.8329827555,-4.2248764431,0.0988037995
H,0,3.0914076647,-2.90716163,0.2351898786

B.4 Located structures and energies for the ring-opening of 1-methylcyclopentoxy radical

Transition structure for the ring-opening of 1-methylcyclopentoxy radical

G4
-0.1529891598D+01 EUMP2

Zero-point correction= 0.156300 (Hartree/Particle)
Thermal correction to Energy= 0.163592
Thermal correction to Enthalpy= 0.164536
Thermal correction to Gibbs Free Energy= 0.124649
Sum of electronic and ZPE= -310.275548
Sum of electronic and thermal Energies= -310.268256
Sum of electronic and thermal Enthalpies= -310.267312
Sum of electronic and thermal Free Energies= -310.307200

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	102.655	27.941	83.950

C,0,1.8371246943,-0.5051040164,2.2869123402
C,0,2.1965734514,0.1498760392,0.9491911651
C,0,1.1266979796,-0.3288259998,-0.0470418174
C,0,-0.217143893,-0.132144366,0.5952218839
C,0,0.3284256508,-0.3560497499,2.5806093802

O,0,-0.3470649658,-1.3714365109,2.8758289341
C,0,-0.0999667138,0.9984126677,3.1626130753
H,0,2.4124195843,-0.0758439868,3.1157735979
H,0,2.0447064741,-1.5791471233,2.2527707454
H,0,3.2082206271,-0.1092051311,0.6214557549
H,0,2.1590955359,1.2430174936,1.0358731401
H,0,1.2832808469,-1.3886067799,-0.2745714337
H,0,1.1904536048,0.2203129606,-0.9965269689
H,0,-0.9819555414,-0.8893299449,0.4633768375
H,0,-0.604386098,0.882954371,0.6370240005
H,0,0.380451641,1.8482977808,2.6700055864
H,0,-1.1850832313,1.1079533096,3.1080968603
H,0,0.1882923532,1.0183589865,4.2207709182

B3LYP/6-31G*

E(UB3LYP) = -310.407434874

Zero-point correction= 0.157685 (Hartree/Particle)
Thermal correction to Energy= 0.164920
Thermal correction to Enthalpy= 0.165864
Thermal correction to Gibbs Free Energy= 0.126075
Sum of electronic and zero-point Energies= -310.249749
Sum of electronic and thermal Energies= -310.242515
Sum of electronic and thermal Enthalpies= -310.241571
Sum of electronic and thermal Free Energies= -310.281360

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	103.489	27.649	83.743

C,0,1.838908287,-0.5104341125,2.2885178514
C,0,2.1940383059,0.1495973744,0.9507716822
C,0,1.1220554343,-0.3237344068,-0.0477618395
C,0,-0.224308007,-0.1346577901,0.5956359289
C,0,0.3326721797,-0.3550950857,2.5935857787
O,0,-0.3459269405,-1.3733504827,2.8979832967
C,0,-0.0967095522,0.9992355046,3.1752772997
H,0,2.4240789809,-0.0883795226,3.1165801231
H,0,2.0408202332,-1.5863343426,2.2471964622
H,0,3.2058809153,-0.1101072774,0.6187084665
H,0,2.1581428569,1.2435733683,1.0425996706
H,0,1.2804632745,-1.3828825091,-0.2822775855
H,0,1.1859789062,0.2332008751,-0.9945378891
H,0,-0.9843566352,-0.8990570275,0.4667501129

H,0,-0.6201190681,0.8788387769,0.6353958789
H,0,0.3812897308,1.8518549209,2.6820080842
H,0,-1.1832898724,1.1061834704,3.1200112408
H,0,0.1898869706,1.0207502664,4.2350784375

Structure for 1-methylcyclopentoxy radical

G4
-0.1520471027D+01 EUMP2

Zero-point correction= 0.158919 (Hartree/Particle)
Thermal correction to Energy= 0.166192
Thermal correction to Enthalpy= 0.167137
Thermal correction to Gibbs Free Energy= 0.127053
Sum of electronic and ZPE= -310.287539
Sum of electronic and thermal Energies= -310.280265
Sum of electronic and thermal Enthalpies= -310.279321
Sum of electronic and thermal Free Energies= -310.319405

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	104.287	27.843	84.364

C,0,-0.0713665553,-0.0513248803,0.2573851281
C,0,1.305693102,-0.0564198175,-0.4439337936
C,0,2.2976687372,-0.5711156109,0.6133140453
C,0,1.7560904127,0.0225612604,1.9157769418
C,0,0.223098372,-0.2034437244,1.8210569778
O,0,-0.0849421299,-1.5155263791,2.0472220239
C,0,-0.6226678574,0.7440956466,2.6810937929
H,0,-1.6867316743,0.5345566681,2.5398739344
H,0,-0.3879044291,0.6033790667,3.7410507349
H,0,-0.7093771457,-0.8770730525,-0.0661187913
H,0,-0.6331117303,0.8737637913,0.1039884607
H,0,1.3031742252,-0.6592422145,-1.3557957356
H,0,1.5736718629,0.965844393,-0.7343040327
H,0,-0.4309334871,1.7911953817,2.4257809756
H,0,3.3334010491,-0.2905618355,0.4033979874
H,0,2.2488548871,-1.6631844996,0.6699016546
H,0,1.963127159,1.0987879802,1.9680622288
H,0,2.1630282021,-0.4420481736,2.8183144671

B3LYP/6-31G*
E(UB3LYP) = -310.423212483

Zero-point correction= 0.160300 (Hartree/Particle)
Thermal correction to Energy= 0.167533
Thermal correction to Enthalpy= 0.168477
Thermal correction to Gibbs Free Energy= 0.128431
Sum of electronic and zero-point Energies= -310.262912
Sum of electronic and thermal Energies= -310.255680
Sum of electronic and thermal Enthalpies= -310.254736
Sum of electronic and thermal Free Energies= -310.294781

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	105.128	27.557	84.283

C,0,-0.0690862506,-0.0303421022,0.2568552046
C,0,0.223605847,-0.1972714609,1.8172507639
C,0,1.7562129184,0.0349952207,1.9125877552
C,0,2.302339237,-0.5694165438,0.6157446141
C,0,1.3064566713,-0.0771922139,-0.4513137331
O,0,-0.0744794225,-1.5206196545,2.033338273
C,0,-0.631389342,0.7298058074,2.6919875014
H,0,1.9585656338,1.1139719706,1.954399007
H,0,2.1660700103,-0.4192891465,2.8210090343
H,0,2.2656477193,-1.6620224339,0.6856420568
H,0,3.3367874602,-0.2796253226,0.4027056799
H,0,1.2922044,-0.712698591,-1.342513248
H,0,1.5846322077,0.9320626131,-0.7794772592
H,0,-0.7418637113,-0.827617102,-0.0722277141
H,0,-0.594519694,0.9191026558,0.1096754797
H,0,-0.4437120388,1.7841092879,2.4586037189
H,0,-1.6948542675,0.5179548983,2.540546944
H,0,-0.4018453785,0.5683351176,3.7512519216

Structure for the product from the 1-methylcyclopentoxy radical ring-opening

G4
-0.1524939671D+01 EUMP2

Zero-point correction= 0.153566 (Hartree/Particle)
Thermal correction to Energy= 0.163226
Thermal correction to Enthalpy= 0.164170
Thermal correction to Gibbs Free Energy= 0.117464
Sum of electronic and ZPE= -310.296497
Sum of electronic and thermal Energies= -310.286838

Sum of electronic and thermal Enthalpies= -310.285893
Sum of electronic and thermal Free Energies= -310.332599

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	102.426	32.416	98.301

C,0,0.4386981705,0.0293924347,-0.1525794812
C,0,0.435135833,-0.1614613789,1.3552605159
H,0,1.1825234849,0.7771639741,-0.4299878331
H,0,-0.5508146559,0.3525936263,-0.4957271646
H,0,0.6563048237,-0.9164792891,-0.6609874482
C,0,-0.5154509663,-1.2228402325,1.8967858789
C,0,-0.5181892638,-1.3345363709,3.4201064062
C,0,-1.4599503913,-2.4313973581,3.9371007263
C,0,-1.4513898697,-2.5727177187,5.4197083528
H,0,-2.260229617,-3.0761178208,5.9365261537
H,0,-0.5715354057,-2.307041773,5.9957027501
H,0,-2.4848878433,-2.2411426078,3.5853208368
H,0,-1.1783697382,-3.3910320307,3.4623458296
H,0,0.5025814502,-1.5289741598,3.7673774314
H,0,-0.7995768543,-0.3693562877,3.8543229834
H,0,-1.5231749258,-1.0048485154,1.5141964993
H,0,-0.242714964,-2.1828586047,1.4335429202
O,0,1.1473717328,0.492764113,2.0819886424

B3LYP/6-31G*

E(UB3LYP) = -310.424970100

Zero-point correction= 0.154863 (Hartree/Particle)
Thermal correction to Energy= 0.164491
Thermal correction to Enthalpy= 0.165435
Thermal correction to Gibbs Free Energy= 0.118752
Sum of electronic and zero-point Energies= -310.270107
Sum of electronic and thermal Energies= -310.260479
Sum of electronic and thermal Enthalpies= -310.259535
Sum of electronic and thermal Free Energies= -310.306218

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	103.219	32.174	98.253

C,0,0.4350490179,0.0359902451,-0.156928274
C,0,0.434053313,-0.1642826479,1.3507816782
H,0,1.1939130415,0.7713404559,-0.4318725644

H,0,-0.5488966393,0.3861262973,-0.494300897
H,0,0.6313733627,-0.9100364114,-0.6764224721
C,0,-0.5128764329,-1.2293596565,1.89488185
C,0,-0.5211626691,-1.3327573253,3.4201841956
C,0,-1.4564940676,-2.4371766355,3.9389570424
C,0,-1.4517754293,-2.5697522087,5.4248480686
H,0,-2.2786734624,-3.0401821683,5.9474822417
H,0,-0.5579381627,-2.3410109792,5.9981831429
H,0,-2.4827659393,-2.2560872764,3.5839743988
H,0,-1.1617018409,-3.3972477327,3.4704572186
H,0,0.5007083242,-1.5171730671,3.7729893777
H,0,-0.8150203639,-0.3675156204,3.8485829545
H,0,-1.5224036786,-1.020567748,1.5084450513
H,0,-0.2307949286,-2.1921217178,1.4399222932
O,0,1.1517375552,0.4929241968,2.0808386939

B.5 Locate structures and energies for the ring-opening of 1-methylcyclobutoxy radical

Transition state structure for the ring-opening of 1-methylcyclobutoxy radical

G4
-0.1303162213D+01 EUMP2

Zero-point correction= 0.127831 (Hartree/Particle)
Thermal correction to Energy= 0.133905
Thermal correction to Enthalpy= 0.134849
Thermal correction to Gibbs Free Energy= 0.097930
Sum of electronic and ZPE= -270.975193
Sum of electronic and thermal Energies= -270.969119
Sum of electronic and thermal Enthalpies= -270.968175
Sum of electronic and thermal Free Energies= -271.005094

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	84.027	22.764	77.703

C,0,0.0115394869,-0.0621010099,0.0102696135
C,0,0.0792366072,-0.1551798365,1.6047983009
C,0,1.5699698551,0.2384402049,1.5655340382
C,0,1.6053453943,-0.1650284475,0.0773298261
H,0,-0.0743046704,-1.1946648176,1.9069008527
H,0,-0.623868242,0.4935382214,2.1277031477

H,0,2.2432682701,-0.2912288767,2.2416500206
H,0,1.7072020965,1.3127445977,1.695775361
H,0,1.9006417367,-1.2074124014,-0.0697191861
H,0,2.1318408098,0.4757498836,-0.6303610484
C,0,-0.7521210351,-1.1443722705,-0.7458526945
H,0,-1.8275610741,-1.0372049064,-0.5706394217
H,0,-0.5764069466,-1.0457553667,-1.8220346269
H,0,-0.4502149247,-2.1500820538,-0.4371806524
O,0,-0.3145253636,1.1948520794,-0.3232635305

HF/6-31G*
E(UHF) = -269.352698786

Zero-point correction= 0.136561 (Hartree/Particle)
Thermal correction to Energy= 0.142628
Thermal correction to Enthalpy= 0.143572
Thermal correction to Gibbs Free Energy= 0.106491
Sum of electronic and ZPE= -269.216137
Sum of electronic and thermal Energies= -269.210071
Sum of electronic and thermal Enthalpies= -269.209126
Sum of electronic and thermal Free Energies= -269.246208

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	89.501	21.776	78.044

C,0,1.5944585629,-0.8080974207,-0.0139206016
C,0,0.3982462657,0.1218241393,-0.0947462597
C,0,-0.8797153327,-0.229002637,1.3103422886
C,0,-1.8678029809,-0.0788179107,0.1635226478
C,0,-0.8255562902,-0.2764474516,-0.942864998
O,0,0.6111083312,1.3638304679,0.0684059339
H,0,-0.760393984,-1.3150308925,-1.2487449741
H,0,-0.944913556,0.3394991227,-1.8265567021
H,0,-2.6895545541,-0.7867860903,0.167193733
H,0,-2.2775298597,0.9226526587,0.1422063995
H,0,-0.6671265167,-1.2359928887,1.6359512297
H,0,-0.860676429,0.4958775117,2.1062334472
H,0,2.1531971687,-0.7596782145,-0.9457082004
H,0,2.2491636578,-0.4954622427,0.7901861906
H,0,1.301426517,-1.8396721517,0.1429298654

B3LYP/6-31G*
E(UB3LYP) = -271.077544320

Zero-point correction= 0.128165 (Hartree/Particle)
Thermal correction to Energy= 0.134550
Thermal correction to Enthalpy= 0.135495
Thermal correction to Gibbs Free Energy= 0.097803
Sum of electronic and zero-point Energies= -270.949380
Sum of electronic and thermal Energies= -270.942994
Sum of electronic and thermal Enthalpies= -270.942050
Sum of electronic and thermal Free Energies= -270.979742

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	84.432	23.406	79.330

C,0,1.5800945238,-0.823938268,0.0048913944
C,0,0.4034530397,0.147429491,-0.0968541537
C,0,-0.8728769334,-0.2179088015,1.3005013847
C,0,-1.8763190252,-0.0957211216,0.1673588965
C,0,-0.8335344248,-0.2687647501,-0.9565114118
O,0,0.6281914188,1.3870101368,0.0650377148
H,0,-0.7589021708,-1.3115149079,-1.2827575802
H,0,-0.9648466774,0.3763729379,-1.8304555673
H,0,-2.6821610496,-0.8378267375,0.1806529073
H,0,-2.3189279577,0.9031579437,0.1478657241
H,0,-0.6176498363,-1.2227816037,1.6361668501
H,0,-0.8122955101,0.5409501949,2.0759696794
H,0,2.1619569953,-0.7649624592,-0.9248073309
H,0,2.2334558766,-0.5290684726,0.8308719419
H,0,1.2646927311,-1.8637375822,0.1364995507

M11/6-31G*
E(UM11) = -270.908054807

Zero-point correction= 0.127894 (Hartree/Particle)
Thermal correction to Energy= 0.134260
Thermal correction to Enthalpy= 0.135204
Thermal correction to Gibbs Free Energy= 0.097658
Sum of electronic and zero-point Energies= -270.780161
Sum of electronic and thermal Energies= -270.773795
Sum of electronic and thermal Enthalpies= -270.772851
Sum of electronic and thermal Free Energies= -270.810397

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin

Total	84.249	23.436	79.021

C,0,1.5847709641,-0.7959233014,0.0107782299
C,0,0.3863760682,0.1416526882,-0.1007105657
C,0,-0.8654804816,-0.2494249234,1.2811899197
C,0,-1.8738402355,-0.0639239184,0.165005265
C,0,-0.8412876262,-0.3037420849,-0.9497330897
O,0,0.5640625349,1.3820197173,0.0617302914
H,0,-0.7710940554,-1.3687101749,-1.2111929893
H,0,-0.9606505341,0.298194408,-1.859315595
H,0,-2.7321044706,-0.7483709389,0.1838367129
H,0,-2.2306310237,0.9719655229,0.1452031779
H,0,-0.6288818359,-1.2794176803,1.5654933628
H,0,-0.776858065,0.4782428754,2.0885699071
H,0,2.1714547028,-0.7240954605,-0.9175923501
H,0,2.2217215423,-0.4757519463,0.8443303576
H,0,1.2867735158,-1.8440187826,0.1468373655

M11/6-31+G**

E(UM11) = -270.928847090

Zero-point correction=	0.127192 (Hartree/Particle)
Thermal correction to Energy=	0.133577
Thermal correction to Enthalpy=	0.134521
Thermal correction to Gibbs Free Energy=	0.096919
Sum of electronic and zero-point Energies=	-270.801655
Sum of electronic and thermal Energies=	-270.795270
Sum of electronic and thermal Enthalpies=	-270.794326
Sum of electronic and thermal Free Energies=	-270.831928

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	83.821	23.539	79.142

C,0,1.576305823,-0.8094074315,0.0147312939
C,0,0.3879594353,0.1390382943,-0.0969163731
C,0,-0.8580219653,-0.2319194659,1.2781176343
C,0,-1.8768508706,-0.0781094972,0.1663458879
C,0,-0.8400217275,-0.2885151202,-0.9524676707
O,0,0.5878173624,1.3810703478,0.0598224216
H,0,-0.7644599296,-1.3460046936,-1.2400762279
H,0,-0.9593337221,0.3371034166,-1.8454451128
H,0,-2.7066125363,-0.7961923151,0.1890051404
H,0,-2.2768136889,0.9416264002,0.1475209132

H,0,-0.6072720189,-1.2530106107,1.581816319
H,0,-0.7716887519,0.5140400198,2.0690565994
H,0,2.1723720575,-0.7239909456,-0.9057034447
H,0,2.205805331,-0.5109620485,0.8613627633
H,0,1.2651462017,-1.8560703504,0.127259856

M11/Aug-cc-pvDZ
E(UM11) = -270.940685108

Zero-point correction= 0.126453 (Hartree/Particle)
Thermal correction to Energy= 0.132862
Thermal correction to Enthalpy= 0.133807
Thermal correction to Gibbs Free Energy= 0.096160
Sum of electronic and zero-point Energies= -270.814232
Sum of electronic and thermal Energies= -270.807823
Sum of electronic and thermal Enthalpies= -270.806879
Sum of electronic and thermal Free Energies= -270.844525

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	83.372	23.662	79.234

C,0,1.5719490327,-0.811119301,0.0180814666
C,0,0.3884852121,0.1421388572,-0.0965708826
C,0,-0.8548605186,-0.2259979419,1.276427324
C,0,-1.876137148,-0.0851595907,0.1654928668
C,0,-0.838534657,-0.2855447656,-0.9541173382
O,0,0.589841034,1.3823514324,0.0581771413
H,0,-0.7568722658,-1.3445392845,-1.2479350317
H,0,-0.9597530892,0.3482013252,-1.8453762243
H,0,-2.6997930477,-0.8154645528,0.1905815297
H,0,-2.289089442,0.9332064291,0.1451784288
H,0,-0.595760806,-1.2466153265,1.5880258323
H,0,-0.7690046587,0.5297833792,2.0636029901
H,0,2.16821951,-0.7315739689,-0.9077676097
H,0,2.2057512385,-0.5125511683,0.8666609411
H,0,1.2498906056,-1.8584195227,0.1339685657

Structure for 1-methylcyclobutoxy radical

G4
-0.1303978457D+01 EUMP2

Zero-point correction= 0.128645 (Hartree/Particle)

Thermal correction to Energy= 0.135147
Thermal correction to Enthalpy= 0.136091
Thermal correction to Gibbs Free Energy= 0.098377
Sum of electronic and ZPE= -270.974646
Sum of electronic and thermal Energies= -270.968144
Sum of electronic and thermal Enthalpies= -270.967200
Sum of electronic and thermal Free Energies= -271.004914

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	84.806	24.312	79.375

C,0,-0.017596232,-0.0549010036,0.0329109212
C,0,0.0635769555,-0.1561249042,1.6041969703
C,0,1.5632773638,0.2201755582,1.5692307065
C,0,1.6058300667,-0.1369937677,0.0719365652
H,0,-0.0974552666,-1.1857874745,1.9349948896
H,0,-0.6175081257,0.5117697599,2.1337476156
H,0,2.2314996846,-0.3414622435,2.2248349362
H,0,1.7218097159,1.2873142408,1.7324060103
H,0,1.8920804091,-1.173188007,-0.1253308034
H,0,2.1133164477,0.5329873085,-0.621217755
C,0,-0.7463257186,-1.1545141896,-0.7356036801
H,0,-1.8260432762,-1.0719882896,-0.5708596699
H,0,-0.5598355311,-1.0496482367,-1.8085978217
H,0,-0.428683091,-2.1517080338,-0.4159398589
O,0,-0.2679014022,1.1863642827,-0.395800025

B3LYP/6-31G*

E(UB3LYP) = -271.083167579

Zero-point correction= 0.129788 (Hartree/Particle)
Thermal correction to Energy= 0.136233
Thermal correction to Enthalpy= 0.137177
Thermal correction to Gibbs Free Energy= 0.099598
Sum of electronic and zero-point Energies= -270.953379
Sum of electronic and thermal Energies= -270.946935
Sum of electronic and thermal Enthalpies= -270.945991
Sum of electronic and thermal Free Energies= -270.983570

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	85.487	24.041	79.092

C,0,1.6733983121,-0.8032021807,0.0024706273
C,0,0.4263623855,0.078881208,0.0204939683
O,0,0.6762862053,1.3944150423,-0.1253386554
C,0,-0.6935364495,-0.1997658643,1.0938494195
C,0,-1.7894935727,-0.019186335,0.0182721651
C,0,-0.7241608232,-0.2326587328,-1.0738963984
H,0,-0.6214416003,-1.2777358428,-1.383655081
H,0,-0.7183057022,0.4195949386,-1.9491816024
H,0,-2.6253348972,-0.7243337934,0.034646667
H,0,-2.182757163,0.9998965534,0.0023323495
H,0,-0.6343966324,-1.2323762158,1.453480477
H,0,-0.689231192,0.4870762174,1.9440200375
H,0,2.2586320877,-0.6068606627,-0.9023644486
H,0,2.3051839241,-0.5757910563,0.8692250703
H,0,1.4190371179,-1.8684282759,0.0355974043

M11/6-31G*

E(UM11) = -270.914607128

Zero-point correction= 0.129424 (Hartree/Particle)
Thermal correction to Energy= 0.135962
Thermal correction to Enthalpy= 0.136906
Thermal correction to Gibbs Free Energy= 0.099135
Sum of electronic and zero-point Energies= -270.785183
Sum of electronic and thermal Energies= -270.778645
Sum of electronic and thermal Enthalpies= -270.777701
Sum of electronic and thermal Free Energies= -270.815473

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	85.318	24.118	79.497

C,0,1.6804088297,-0.7769634405,-0.0001808069
C,0,0.4091064927,0.0597587614,0.0097238718
O,0,0.617083501,1.391601511,-0.1027583007
C,0,-0.6970378632,-0.2259545838,1.0841376509
C,0,-1.7832793407,0.012557047,0.0162489824
C,0,-0.7214559449,-0.2660305424,-1.0625546685
H,0,-0.6519040097,-1.3317209742,-1.3202036634
H,0,-0.7008891024,0.347980634,-1.9698656797
H,0,-2.6657485408,-0.6376802785,0.0351838673
H,0,-2.0975634586,1.062039299,-0.0033403793
H,0,-0.651569563,-1.2792545678,1.3936055757
H,0,-0.6715824315,0.4270204619,1.9645543162

H,0,2.2634331706,-0.5606322093,-0.905792971
H,0,2.3004862376,-0.531807088,0.8735865314
H,0,1.4507540232,-1.8513890298,0.027607674

M11/6-31+G**

E(UM11) = -270.933652552

Zero-point correction= 0.128577 (Hartree/Particle)
Thermal correction to Energy= 0.135089
Thermal correction to Enthalpy= 0.136034
Thermal correction to Gibbs Free Energy= 0.098372
Sum of electronic and zero-point Energies= -270.805076
Sum of electronic and thermal Energies= -270.798563
Sum of electronic and thermal Enthalpies= -270.797619
Sum of electronic and thermal Free Energies= -270.835280

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	84.770	24.288	79.265

C,0,1.6758109741,-0.7854801683,0.0006941473
C,0,0.4148940857,0.0657199521,0.0151575842
O,0,0.6365567344,1.3914381726,-0.1090149648
C,0,-0.6954729152,-0.2166798683,1.0854379968
C,0,-1.7854327713,0.0019034954,0.016404664
C,0,-0.7209226597,-0.2529899139,-1.0649538689
H,0,-0.6341544206,-1.3138239129,-1.3359771166
H,0,-0.7026417973,0.3758572495,-1.9616218854
H,0,-2.6507083676,-0.6709090693,0.0338139969
H,0,-2.1292549038,1.0420774488,-0.0008750306
H,0,-0.6405600556,-1.2655093743,1.4074486158
H,0,-0.6759411694,0.4478469433,1.9570565169
H,0,2.2545423098,-0.5809933232,-0.9097620775
H,0,2.3025333852,-0.5430458457,0.8698534793
H,0,1.4309935715,-1.8558867857,0.0362899426

M11/AUG-cc-pvDZ

E(UM11) = -270.945145593

Zero-point correction= 0.127789 (Hartree/Particle)
Thermal correction to Energy= 0.134334
Thermal correction to Enthalpy= 0.135278
Thermal correction to Gibbs Free Energy= 0.097562
Sum of electronic and zero-point Energies= -270.817357

Sum of electronic and thermal Energies= -270.810812
Sum of electronic and thermal Enthalpies= -270.809868
Sum of electronic and thermal Free Energies= -270.847583

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	84.296	24.446	79.379

C,0,1.6724931526,-0.7871174222,0.000739206
C,0,0.4166846356,0.0697985635,0.0165239932
O,0,0.6380854183,1.3921619544,-0.1118195494
C,0,-0.6944571706,-0.2139218816,1.0862644167
C,0,-1.7850057611,-0.0023013873,0.0167235833
C,0,-0.7202318247,-0.2496090921,-1.0655162999
H,0,-0.6251539618,-1.3125969389,-1.339734478
H,0,-0.7014491769,0.3858253824,-1.9618262485
H,0,-2.6489510825,-0.6826550237,0.0337815106
H,0,-2.1360077037,1.039180657,-0.0004716888
H,0,-0.6340146503,-1.2650870091,1.41186598
H,0,-0.6755892409,0.45689926,1.9574908085
H,0,2.2531144201,-0.584802211,-0.9138804719
H,0,2.3028728712,-0.5467817734,0.8730492359
H,0,1.4178520746,-1.859468078,0.0367620024

Structure for the product from the 1-methylcyclobutoxy radical ring-opening

B3LYP/6-31G*
E(UB3LYP) = -271.111305304

Zero-point correction= 0.126385 (Hartree/Particle)
Thermal correction to Energy= 0.134813
Thermal correction to Enthalpy= 0.135757
Thermal correction to Gibbs Free Energy= 0.091674
Sum of electronic and zero-point Energies= -270.984920
Sum of electronic and thermal Energies= -270.976492
Sum of electronic and thermal Enthalpies= -270.975548
Sum of electronic and thermal Free Energies= -271.019631

	E (Thermal) KCal/Mol	CV Cal/Mol-Ke lvin	S Cal/Mol-Kelvin
Total	84.597	27.385	92.781

C,0,0.522618738,0.0325169935,-0.1285297571
C,0,0.4223852116,-0.1722177046,1.3754756125

O,0,1.0947975836,0.4773403167,2.1535151398
C,0,-0.5665250964,-1.232500226,1.8518433816
C,0,-0.6632615639,-1.3386027535,3.3899736249
C,0,-1.6163003362,-2.3932771337,3.8432468545
H,0,1.2983982065,0.7682104842,-0.3504152637
H,0,-0.4370180476,0.3836098919,-0.5287710838
H,0,0.7527120977,-0.9122739281,-0.636139161
H,0,-2.6678967603,-2.1715880825,3.9981941285
H,0,-1.3148985127,-3.4358905289,3.8870063667
H,0,0.3444014151,-1.5324142216,3.7781273469
H,0,-0.9558321384,-0.3573094244,3.782250518
H,0,-1.5510114594,-1.0141172892,1.4131979973
H,0,-0.2683793374,-2.1976933937,1.4160202948

M11/6-31G*

E(UM11) = -270.941061971

Zero-point correction= 0.126070 (Hartree/Particle)
Thermal correction to Energy= 0.134352
Thermal correction to Enthalpy= 0.135296
Thermal correction to Gibbs Free Energy= 0.092358
Sum of electronic and zero-point Energies= -270.814992
Sum of electronic and thermal Energies= -270.806710
Sum of electronic and thermal Enthalpies= -270.805766
Sum of electronic and thermal Free Energies= -270.848703

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	84.307	27.394	90.370

C,0,1.3577284261,0.4342152369,-0.6304111441
C,0,0.1672578768,-0.3037443248,-0.0470659532
C,0,-3.3838144318,-1.3586617877,-1.1504725576
C,0,-2.2139618393,-1.1562515074,-0.2514865134
C,0,-1.0431808672,-0.4688040528,-0.9527945429
O,0,0.1754712585,-0.7363804389,1.0857700609
H,0,-1.3367110405,0.5238755064,-1.3325865206
H,0,-0.7282099677,-1.0418569656,-1.8421711911
H,0,-2.4985878989,-0.5718413585,0.6369285194
H,0,-1.8513811109,-2.1194424367,0.1558921914
H,0,-3.2398323555,-1.5370587677,-2.2157669548
H,0,-4.3784325421,-1.5261474096,-0.7429246134
H,0,2.187216241,0.4175095385,0.0841557243
H,0,1.66952638,-0.0242798564,-1.5798284949

H,0,1.0799808715,1.4761836244,-0.84756201

B.6 Located structures and energies for the ring-opening of 1-phenylcyclopropoxy radical

Transition state structures for the ring-opening of 1-phenylcyclopropoxy radical

B3LYP/6-31G*

E(UB3LYP) = -423.516301466

Zero-point correction=	0.152918 (Hartree/Particle)
Thermal correction to Energy=	0.161018
Thermal correction to Enthalpy=	0.161962
Thermal correction to Gibbs Free Energy=	0.119135
Sum of electronic and zero-point Energies=	-423.363383
Sum of electronic and thermal Energies=	-423.355283
Sum of electronic and thermal Enthalpies=	-423.354339
Sum of electronic and thermal Free Energies=	-423.397166

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	101.040	32.215	90.137

C,0,1.9741128095,0.2032349295,-0.5862982523
C,0,0.6885680236,0.4189062788,-0.0675814392
C,0,0.4446947937,0.1021120824,1.2779889478
C,0,1.4604209037,-0.4136967854,2.0824508206
C,0,2.7357556483,-0.6251035183,1.5555550147
C,0,2.987329376,-0.3145485244,0.2171814469
C,0,-0.3502126271,0.9659644488,-1.0051145541
O,0,-0.0747847739,1.2101408977,-2.2198441716
C,0,-1.8620696279,0.8775482934,-0.6158435646
C,0,-1.3675431035,2.2068888233,-0.2900505669
H,0,-0.5384700976,0.2572249851,1.7148258261
H,0,1.2529692389,-0.6522421132,3.1223064003
H,0,3.5259991677,-1.0285905764,2.1828737592
H,0,3.9769411357,-0.4760999424,-0.2023384047
H,0,2.1544686387,0.4479981431,-1.6275706176
H,0,-2.4926836428,0.7718157118,-1.4934402557
H,0,-2.0943889525,0.1937430122,0.1969397333
H,0,-1.4967224698,3.0216189564,-0.9916368354

H,0,-1.0557694409,2.4563038975,0.717800713

M11/6-31+G**
E(UM11) = -423.282736949

Zero-point correction=	0.152480 (Hartree/Particle)
Thermal correction to Energy=	0.160560
Thermal correction to Enthalpy=	0.161505
Thermal correction to Gibbs Free Energy=	0.118776
Sum of electronic and zero-point Energies=	-423.130257
Sum of electronic and thermal Energies=	-423.122176
Sum of electronic and thermal Enthalpies=	-423.121232
Sum of electronic and thermal Free Energies=	-423.163961

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	100.753	32.198	89.930

C,0,1.9705209561,0.1905251958,-0.5967460665
C,0,0.6896106066,0.3989878552,-0.0805307971
C,0,0.4352195207,0.1001601966,1.2616942802
C,0,1.4493647056,-0.3988545959,2.0750463369
C,0,2.7257763735,-0.6061826421,1.5542827979
C,0,2.982657359,-0.3106232766,0.2160253054
C,0,-0.3535924222,0.9278111616,-1.0279075665
O,0,-0.0696068945,1.2052337989,-2.2165050926
C,0,-1.8457015532,0.8785836016,-0.6148746573
C,0,-1.3749011116,2.2083820912,-0.2540316511
H,0,-0.5570663774,0.2581914592,1.6904561767
H,0,1.2404168885,-0.6268002191,3.1212113618
H,0,3.5188151722,-0.9986386644,2.1923008158
H,0,3.9795661492,-0.4713278775,-0.1970856269
H,0,2.1455971371,0.4295752295,-1.6462999149
H,0,-2.4842219845,0.7985375721,-1.4945275344
H,0,-2.0773337421,0.178513699,0.1898181052
H,0,-1.4804526976,3.0307581953,-0.9570440583
H,0,-1.0260530854,2.4303842195,0.7529217856

Structure of 1-phenylcyclopropoxy radical

B3LYP/6-31G*
E(UB3LYP) = -423.516894888

Zero-point correction=	0.153710 (Hartree/Particle)

Thermal correction to Energy= 0.162173
Thermal correction to Enthalpy= 0.163117
Thermal correction to Gibbs Free Energy= 0.119681
Sum of electronic and zero-point Energies= -423.363184
Sum of electronic and thermal Energies= -423.354722
Sum of electronic and thermal Enthalpies= -423.353778
Sum of electronic and thermal Free Energies= -423.397213

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	101.765	33.736	91.419

C,0,0.0950290836,0.3529143229,0.1304538258
C,0,-0.2393486272,-0.4371297196,1.3656248463
O,0,0.6557470706,-1.1561456325,1.9454764284
C,0,-1.7487496525,-0.9847250267,1.5245447305
C,0,-1.3729203335,0.1505215555,2.3522486738
H,0,-1.7112474172,1.1483831113,2.0904978983
H,0,-1.1250460483,-0.0127249812,3.3949335184
H,0,-1.7749062357,-1.9754379391,1.9639660548
H,0,-2.367578918,-0.8338347983,0.6453464193
C,0,-0.8286895311,1.1578446813,-0.5539342816
C,0,-0.4491742741,1.8643840631,-1.6950737026
C,0,0.8598623351,1.77874047,-2.171937754
C,0,1.7858926838,0.9801307654,-1.4972428535
C,0,1.4073923576,0.2740660145,-0.3571996858
H,0,-1.8550121737,1.2431711651,-0.2049597614
H,0,-1.1791054637,2.4824947663,-2.2112697236
H,0,1.1549168886,2.3294290433,-3.0610270335
H,0,2.8077909086,0.9065818218,-1.8603228811
H,0,2.1174403472,-0.3494776832,0.1754792813

M11/6-31+G**
E(UM11) = -423.284348459

Zero-point correction= 0.153464 (Hartree/Particle)
Thermal correction to Energy= 0.161824
Thermal correction to Enthalpy= 0.162768
Thermal correction to Gibbs Free Energy= 0.119625
Sum of electronic and zero-point Energies= -423.130884
Sum of electronic and thermal Energies= -423.122524
Sum of electronic and thermal Enthalpies= -423.121580
Sum of electronic and thermal Free Energies= -423.164724

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	101.546	33.526	90.803

C,0,0.1000411554,0.3503646304,0.1317327619
C,0,-0.2372119504,-0.4391932105,1.367604965
O,0,0.6484708108,-1.1544651207,1.9465650275
C,0,-1.7471094503,-0.9737439026,1.5129782482
C,0,-1.3725563329,0.1577118119,2.3378967033
H,0,-1.6859883836,1.1638325434,2.0594336868
H,0,-1.1247018041,-0.0089061576,3.3840972053
H,0,-1.7728848331,-1.966839931,1.9566294352
H,0,-2.342713392,-0.8198970952,0.613176868
C,0,-0.8295654786,1.1491311575,-0.5414977174
C,0,-0.4560963427,1.8566759715,-1.6813170082
C,0,0.850358966,1.773201288,-2.1600597325
C,0,1.7798285269,0.977845928,-1.4914133063
C,0,1.4072863014,0.2702420842,-0.3519144961
H,0,-1.8590935583,1.228772846,-0.1832033849
H,0,-1.1906686848,2.4764060057,-2.1975965484
H,0,1.1422199212,2.3276688147,-3.0529151015
H,0,2.8041494543,0.9078842193,-1.8605673599
H,0,2.1185280747,-0.3575068829,0.1859727538

Structure for the product from the 1-phenylcyclopropoxy radical ring-opening

B3LYP/6-31G*
E(UB3LYP) = -423.537262074

Zero-point correction= 0.151829 (Hartree/Particle)
Thermal correction to Energy= 0.161213
Thermal correction to Enthalpy= 0.162157
Thermal correction to Gibbs Free Energy= 0.116351
Sum of electronic and zero-point Energies= -423.385433
Sum of electronic and thermal Energies= -423.376049
Sum of electronic and thermal Enthalpies= -423.375105
Sum of electronic and thermal Free Energies= -423.420911

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	101.163	35.322	96.407

C,0,0.6459288291,0.8623663579,0.1621544803

C,0,0.4334683796,0.4516472765,1.4873643787
C,0,1.3390371296,-0.4027490235,2.1158167899
C,0,2.465967907,-0.8558784476,1.427628534
C,0,2.6862669756,-0.4523448335,0.1072851739
C,0,1.7830444333,0.4000189791,-0.5198612689
H,0,-0.4373530323,0.7943286482,2.0371903174
H,0,1.1647024415,-0.71434834,3.1420159386
H,0,3.1709572894,-1.5216852071,1.9183878325
H,0,3.5628500568,-0.8039266225,-0.4301192174
H,0,1.9339982178,0.7259624519,-1.5437377055
C,0,-0.2885585868,1.7791798285,-0.5712054244
C,0,-1.533141176,2.2919242089,0.1581794836
C,0,-2.3826365081,3.190702444,-0.6660532221
O,0,-0.0577218332,2.1067370654,-1.7245809806
H,0,-2.1040023715,1.4165613754,0.5163221655
H,0,-1.2034107457,2.7910950775,1.0868932426
H,0,-3.2903986377,3.612898262,-0.2499609416
H,0,-2.0983657683,3.426386499,-1.6834005763

M11/6-31+G**

E(UM11) = -423.298359303

Zero-point correction= 0.151255 (Hartree/Particle)
Thermal correction to Energy= 0.160702
Thermal correction to Enthalpy= 0.161646
Thermal correction to Gibbs Free Energy= 0.115498
Sum of electronic and zero-point Energies= -423.147104
Sum of electronic and thermal Energies= -423.137658
Sum of electronic and thermal Enthalpies= -423.136714
Sum of electronic and thermal Free Energies= -423.182862

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	100.842	35.398	97.127

C,0,0.6480743955,0.8602512572,0.163491275
C,0,0.4290582102,0.4559727299,1.4835489189
C,0,1.3332812112,-0.3974068062,2.111899866
C,0,2.4580040658,-0.8491012479,1.4240986586
C,0,2.679909505,-0.4475643417,0.1060836083
C,0,1.7777994779,0.4039855968,-0.5211946924
H,0,-0.447790555,0.8029804157,2.032147336
H,0,1.1585710986,-0.7103774806,3.1419672592
H,0,3.1652434192,-1.5174331926,1.9176359057

H,0,3.5603270602,-0.8013035366,-0.4319370391
H,0,1.9245961628,0.7348299947,-1.5502464662
C,0,-0.2909521693,1.7797410025,-0.5692021857
C,0,-1.5271208219,2.2856400261,0.1638902249
C,0,-2.3736627193,3.1830200573,-0.661551672
O,0,-0.0600707965,2.1049985701,-1.717603369
H,0,-2.0937657847,1.4032827884,0.5165902566
H,0,-1.1876327353,2.7859317703,1.0904362265
H,0,-3.2842871213,3.6083040134,-0.2479724154
H,0,-2.0789519032,3.413122383,-1.6817636959

B.7 Potential Energies from Single Point Calculations on B3LYP/6-31G* optimized structures for 1-methylcyclopentoxy radical cleavage.

These energies were utilized to compare methods agains UCCSD(T) calculations by calculating the root mean square error.

	UCCSD(T)				
C-C Distance	6-31G*	6-31+G**	6-311+G**	cc-pvdz	aug-cc-pvdz
1.597	-3.09E+02	-3.10E+02	-3.10E+02	-3.10E+02	-3.10E+02
1.7	-3.09E+02	-3.10E+02	-3.10E+02	-3.10E+02	-3.10E+02
1.8	-3.09E+02	-3.10E+02	-3.10E+02	-3.10E+02	-3.10E+02
1.9	-3.09E+02	-3.10E+02	-3.10E+02	-3.10E+02	-3.10E+02
2	-3.09E+02	-3.10E+02	-3.10E+02	-3.10E+02	-3.10E+02
2.1	-3.09E+02	-3.10E+02	-3.10E+02	-3.10E+02	-3.10E+02
2.3	-3.09E+02	-3.10E+02	-3.10E+02	-3.10E+02	-3.10E+02
2.5	-3.09E+02	-3.10E+02	-3.10E+02	-3.10E+02	-3.10E+02
3.23		-3.10E+02	-3.10E+02	-3.10E+02	-3.10E+02

	UB3LYP		
C-C Distance	6-31G*	6-31+G**	6-311+G**
1.597	-310.4232126	-310.4501463	-310.5129298
1.7	-310.421025	-310.4482184	-310.5110498
1.8	-310.4165732	-310.4440967	-310.5070852
1.9	-310.4120446	-310.439958	-310.5031789
2	-310.4089951	-310.4372674	-310.5007783
2.1	-310.4081755	-310.4366724	-310.5004867
2.3	-310.4114278	-310.4400251	-310.5043096
2.5	-310.4163728	-310.4449599	-310.5095165
3.23	-310.4241462	-310.453167	-310.5179694

	GD3	UM062X		
C-C Distance	/	6-31G*	6-31+G**	6-311+G**
1.597	-310.4373358	-310.2693881	-310.2904071	-310.3600266
1.7	-310.4351205	-310.2657652	-310.2870032	-310.3567138
1.8	-310.4306813	-310.2598383	-310.2813911	-310.3512456
1.9	-310.4262268	-310.2541065	-310.2760618	-310.3461017
2	-310.4233949	-310.2503479	-310.2726768	-310.3429598
2.1	-310.4228747	-310.2495047	-310.2720657	-310.342644
2.3	-310.4263525	-310.2543398	-310.2769843	-310.3480142
2.5	-310.4311687	-310.2602163	-310.2828761	-310.3541954
3.23	-310.4374486	-310.2660708	-310.2894292	-310.361079

	UM06		
C-C Distance	6-31G*	6-31+G**	6-311+G**
1.597	-310.1951178	-310.218499	-310.2770164
1.7	-310.1922853	-310.2158981	-310.27429
1.8	-310.1875826	-310.211477	-310.2698284
1.9	-310.1831635	-310.2073654	-310.265827
2	-310.1806083	-310.2051056	-310.2638359
2.1	-310.1807232	-310.2054057	-310.2644895
2.3	-310.1860352	-310.2106941	-310.2703229
2.5	-310.1920773	-310.216702	-310.2766424
3.23	-310.1961173	-310.2211602	-310.2813022

	UM11		
C-C Distance	6-31+G**	6-31G**	6-31G*
1.597	-310.2503445	-310.3555004	-310.2292802
1.7	-310.24728	-310.3514432	-310.2259302
1.8	-310.2422362	-310.3455018	-310.2204575
1.9	-310.2377506	-310.3403709	-310.2154228
2	-310.2353273	-310.3376332	-310.2125464
2.1	-310.235311	-310.3382146	-310.2123254
2.3	-310.2390581	-310.344863	-310.2161683
2.5	-310.2438006	-310.3507134	-310.2210217
3.23	-310.25005	-310.3561184	-310.2268437

B.8 Potential Energies from Single Point Calculations on B3LYP/6-31G* optimized structures for 1-methylcyclobutoxy radical cleavage.

These potential energies were utilized to compare methods agains UCCSD(T) calculations by calculating the root mean square error.

	UCCSD(T)		
C-C Distance	6-31G*	6-31+G**	6-311+G**
1.57	-2.31E+02	-2.31E+02	-2.31E+02
1.7	-2.31E+02	-2.31E+02	-2.31E+02
1.8	-2.31E+02	-2.31E+02	-2.31E+02
1.9	-2.31E+02	-2.31E+02	-2.31E+02
2	-2.31E+02	-2.31E+02	-2.31E+02
2.1	-2.31E+02	-2.31E+02	-2.31E+02
2.3	-2.31E+02	-2.31E+02	-2.31E+02
2.5	-2.31E+02	-2.31E+02	-2.31E+02
4.32	-2.31E+02	-2.31E+02	-2.31E+02

	UCCSD(T)			
C-C Distance	cc-pvdz	aug-cc-pvdz	cc-pvtz	aug-cc-pvtz
1.57	-2.31E+02	-2.31E+02	-2.31E+02	-2.31E+02
1.7	-2.31E+02	-2.31E+02	-2.31E+02	
1.8	-2.31E+02	-2.31E+02	-2.31E+02	-2.31E+02
1.9	-2.31E+02	-2.31E+02	-2.31E+02	-2.31E+02
2	-2.31E+02	-2.31E+02	-2.31E+02	-2.31E+02
2.1	-2.31E+02	-2.31E+02	-2.31E+02	-2.31E+02
2.3	-2.31E+02	-2.31E+02	-2.31E+02	-2.31E+02
2.5	-2.31E+02	-2.31E+02	-2.31E+02	-2.31E+02
4.32	-2.31E+02	-2.31E+02	-2.31E+02	-2.31E+02

	UM062X				
C-C Distance	6-31G*	6-31+G**	6-311+G**	aug-cc-pvdz	cc-pvtz
1.57	-231.6472777	-231.6634232	-231.7174204	-231.6849232	-231.7370655
1.7	-231.6445516	-231.6611095	-231.7152964	-231.6827489	-231.7349391
1.8	-231.6401932	-231.6573089	-231.7117529	-231.6791356	-231.7315467
1.9	-231.6372059	-231.6548297	-231.7095799	-231.6768567	-231.7296747
2	-231.6374353	-231.6553031	-231.7103748	-231.6774698	-231.7307345
2.1	-231.6407525	-231.6586406	-231.7139572	-231.680799	
2.3	-231.6501333	-231.6679514	-231.723595	-231.6899503	
2.5	-231.6579379	-231.6758439	-231.7316654	-231.6976447	
4.32	-231.6662834	-231.6844392	-231.7403484	-231.7058422	

	UMP4		
C-C Distance	cc-pvdz	aug-cc-pvdz	cc-pvtz
1.57	-2.31E+02	-2.31E+02	-2.31E+02
1.7	-2.31E+02	-2.31E+02	-2.31E+02
1.8	-2.31E+02	-2.31E+02	-2.31E+02
1.9	-2.31E+02	-2.31E+02	-2.31E+02
2	-2.31E+02	-2.31E+02	-2.31E+02
2.1	-2.31E+02	-2.31E+02	-2.31E+02
2.3	-2.31E+02	-2.31E+02	-2.31E+02
2.5	-2.31E+02	-2.31E+02	-2.31E+02
4.32	-2.31E+02	-2.31E+02	-2.31E+02

	UMP2		
C-C Distance	aug-cc-pvdz	cc-pvtz	aug-cc-pvtz
1.57	-2.31E+02	-2.31E+02	-2.31E+02
1.7	-2.31E+02	-2.31E+02	-2.31E+02
1.8	-2.31E+02	-2.31E+02	-2.31E+02
1.9	-2.31E+02	-2.31E+02	-2.31E+02
2	-2.31E+02	-2.31E+02	-2.31E+02
2.1	-2.31E+02	-2.31E+02	-2.31E+02
2.3	-2.31E+02	-2.31E+02	-2.31E+02
2.5	-2.31E+02	-2.31E+02	-2.31E+02
4.32	-2.31E+02	-2.31E+02	-2.31E+02

	UB3LYP	
C-C Distance	6-31G*	6-31+G**
1.57	-231.7629255	-231.7835984
1.7	-231.7616501	-231.7827779
1.8	-231.758758	-231.78045
1.9	-231.7567601	-231.7789521
2	-231.7571761	-231.7796284
2.1	-231.7598163	-231.7822921
2.3	-231.7676474	-231.7900199
2.5	-231.7746484	-231.7970342
4.32	-231.7841188	-231.806854

	UM11		
C-C Distance	6-31+G**	6-31G**	6-31G*
1.57	-231.637973	-231.7032928	-231.6215254
1.7	-231.6362035	-231.7008675	-231.6192587
1.8	-231.633406	-231.6975086	-231.6157504
1.9	-231.6320387	-231.6960344	-231.6138232
2	-231.6330637	-231.6979383	-231.6146655
2.1	-231.6359721	-231.7024669	-231.6176637
2.3	-231.6439069	-231.7120898	-231.6258167
2.5	-231.651092	-231.7189936	-231.6329789
4.32	-231.6594081	-231.7271767	-231.6409996

B.9 Located structures and energies for iminium catalyzed Diels-Alder reaction

B3LYP/6-31G* transition structure for the Diels-Alder cycloaddition between cyclopentadiene and *trans*-cinnamaldehyde.

Parent compound (endo)

E(RB3LYP) = -1231.99541970

Zero-point correction= 0.521978 (Hartree/Particle)
Thermal correction to Energy= 0.549682
Thermal correction to Enthalpy= 0.550626
Thermal correction to Gibbs Free Energy= 0.461041
Sum of electronic and ZPE= -1231.473441
Sum of electronic and thermal Energies= -1231.445738
Sum of electronic and thermal Enthalpies= -1231.444794
Sum of electronic and thermal Free Energies= -1231.534379

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	344.930	108.173	188.548

C,0,-0.4052946572,2.3177121027,0.5480828249
C,0,-1.9941501115,0.6258864948,-0.3267167364
H,0,-2.0341460451,0.3350029082,-1.3826854105
N,0,-1.7580751157,2.850461704,0.372696573
C,0,-2.6761604878,1.9780718892,-0.1483668457
O,0,-3.8413971926,2.2222215826,-0.3951135501
N,0,-0.5936373988,0.9140508483,0.0550012986
C,0,-2.1159409012,4.230009137,0.6710710942
H,0,-3.1811422542,4.3285735419,0.4566408308
H,0,-1.9396314108,4.4684856496,1.7247392405

H,0,-1.5613236982,4.9347526036,0.043098208
C,0,-0.0060513851,2.3354026934,2.0341517271
H,0,0.9816105746,1.8959929619,2.1949099866
H,0,0.0336600601,3.3662772553,2.3973730672
H,0,-0.7405445787,1.7869644257,2.6312564817
C,0,0.5908971193,3.0878188947,-0.3365347142
H,0,0.658303086,4.1252797456,0.0026162818
H,0,1.5956924934,2.6633249466,-0.2940641864
H,0,0.2534262141,3.0835501573,-1.3767963411
C,0,0.3566647462,-0.0062502882,-0.1292859245
C,0,1.7095876798,0.01052192,0.1812872648
H,0,2.1313506258,0.8539113316,0.7099603858
H,0,-0.0160331118,-0.898719514,-0.6305712283
C,0,2.6245320998,-0.9709853312,-0.3831873231
H,0,2.1649230544,-1.5564861316,-1.1786532852
C,0,3.9878556835,-0.5000206722,-0.8215040706
C,0,4.552362249,-1.0687442014,-1.9734872821
C,0,4.7237639441,0.4688124159,-0.1218709289
C,0,5.8121035203,-0.6740301421,-2.4223179256
H,0,3.9969471826,-1.8206829907,-2.5297496648
C,0,5.9847566966,0.8615913207,-0.5683242764
H,0,4.3210029064,0.934449976,0.7738931165
C,0,6.5333252314,0.2920511296,-1.7195066425
H,0,6.2270176409,-1.119860235,-3.3213919611
H,0,6.5384018227,1.616176612,-0.0172982181
H,0,7.514978161,0.6006992687,-2.065919041
C,0,-2.6529162118,-0.4875488308,0.5366385432
H,0,-2.858242726,-0.0850356884,1.5354194108
H,0,-1.9102314854,-1.2858016187,0.6636326915
C,0,-3.9073400823,-1.0726182445,-0.0791192627
C,0,-5.1776662036,-0.5908420127,0.2578845275
C,0,-3.8055936556,-2.118320672,-1.0067580807
C,0,-6.3202523126,-1.143600604,-0.3206343938
H,0,-5.2731832771,0.2283017193,0.9638142929
C,0,-4.9459925094,-2.6702460733,-1.5897666076
H,0,-2.8253505141,-2.5137123137,-1.2709706954
C,0,-6.208016207,-2.18283158,-1.2455921457
H,0,-7.2992406533,-0.7597146479,-0.048846318
H,0,-4.8501875552,-3.4830788069,-2.3041740503
H,0,-7.098971868,-2.612703974,-1.6940867273
C,0,2.8613427888,-1.5345333507,2.2069316937
H,0,3.3107610612,-0.5433444274,2.2638924416
H,0,3.3537497276,-2.1556104541,2.9740425916
C,0,1.3888372111,-1.6007739291,2.4393484854

H,0,0.8557259398,-1.0079094676,3.1745582342
C,0,0.8616886618,-2.6730572362,1.7290415369
H,0,-0.1476844173,-3.058199694,1.8194107033
C,0,2.981458216,-2.2687577247,0.8717753443
H,0,3.9461033133,-2.6609113618,0.5612673989
C,0,1.8416865544,-3.1400325661,0.8459770725
H,0,1.7191737614,-3.9719574512,0.1591814885

Parent Compound (exo)
E(RB3LYP) = -1231.99662790

Zero-point correction= 0.521744 (Hartree/Particle)
Thermal correction to Energy= 0.549568
Thermal correction to Enthalpy= 0.550512
Thermal correction to Gibbs Free Energy= 0.460507
Sum of electronic and ZPE= -1231.474884
Sum of electronic and thermal Energies= -1231.447060
Sum of electronic and thermal Enthalpies= -1231.446115
Sum of electronic and thermal Free Energies= -1231.536121

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	344.859	108.324	189.433

C,0,-1.1021171586,2.4977324736,0.2138509329
C,0,-2.6846967178,0.7077644589,-0.4495946363
H,0,-2.6478516624,0.2650761896,-1.4517974384
N,0,-2.4230219492,3.0181776545,-0.150525898
C,0,-3.3371046004,2.082083722,-0.5421814218
O,0,-4.4887099654,2.2930386377,-0.8786401165
N,0,-1.3103221769,1.0304666657,-0.0085780901
C,0,-2.7580296807,4.4352290301,-0.1173192779
H,0,-3.8084583014,4.5149358367,-0.4009278323
H,0,-2.6260557776,4.8514224559,0.886334265
H,0,-2.1534696404,5.0070442262,-0.8286513789
C,0,-0.7929064069,2.7924813277,1.6917791862
H,0,0.1446161906,2.3281520186,2.0071058664
H,0,-0.6954001607,3.8706018753,1.8482315048
H,0,-1.6019461859,2.4218949721,2.3282261868
C,0,-0.0298558034,3.0589342561,-0.736403397
H,0,0.0357946351,4.144067915,-0.617243411
H,0,0.9602272381,2.6468333282,-0.5326102951
H,0,-0.2932921258,2.838652378,-1.7747381624
C,0,-0.3870763951,0.0653312676,0.0580631781

C,0,0.9444997904,0.1085956467,0.4428423312
H,0,1.3784896407,1.0321142001,0.8008245932
H,0,-0.7693254742,-0.8963429638,-0.2826325374
C,0,1.8174126887,-1.0154544001,0.1981767872
H,0,1.3226738647,-1.8121749761,-0.3605366981
C,0,3.2062757713,-0.7860686226,-0.316835836
C,0,3.7376910999,-1.6987317863,-1.2402392009
C,0,3.9947742228,0.3053475951,0.080518031
C,0,5.019536762,-1.5226727447,-1.7628089811
H,0,3.1401359365,-2.5493423871,-1.5611368157
C,0,5.2754089807,0.4807184218,-0.4389145654
H,0,3.6155893492,1.0268847909,0.8000916396
C,0,5.7919573007,-0.4325053546,-1.3631901754
H,0,5.4107905535,-2.236542409,-2.4814377326
H,0,5.8717596046,1.3323674822,-0.1247420905
C,0,-3.4589747714,-0.2515632464,0.5077673499
H,0,-4.087849072,0.3522505298,1.1729598684
H,0,-2.7289942887,-0.7601840624,1.1483172946
C,0,-4.2965287964,-1.2910974992,-0.2124089426
C,0,-5.3320293472,-0.9108954244,-1.0791524572
C,0,-4.0441144187,-2.6545793246,-0.0171437496
C,0,-6.0914065648,-1.8800294383,-1.7349241743
H,0,-5.5383611137,0.1444335373,-1.2354278113
C,0,-4.8074934949,-3.6243413803,-0.6698054578
H,0,-3.2531426737,-2.9653646126,0.6640464815
C,0,-5.8330008703,-3.2377886597,-1.5327106537
H,0,-6.8917107425,-1.57245409,-2.4021158211
H,0,-4.6026036822,-4.6780554255,-0.5016716111
H,0,-6.4297097379,-3.9891687995,-2.0418381458
C,0,2.6482647365,-1.1699143698,2.7347701743
H,0,3.7183433652,-1.008546307,2.8033571058
C,0,1.6739246297,-0.4672102997,3.4719316999
H,0,1.8717769999,0.3396988899,4.1682680021
C,0,0.4279345041,-0.956061993,3.1307452302
H,0,-0.5217428296,-0.5916961019,3.5068798049
C,0,2.0211146654,-2.0318079149,1.7940187868
H,0,2.5628963343,-2.8920817521,1.4092514127
C,0,0.5883001882,-2.1815561456,2.2938292694
H,0,-0.1826893969,-2.3401737753,1.5378348975
H,0,0.5627397016,-3.0585604042,2.962330727
H,0,6.7902502296,-0.2928901125,-1.766759794

4-methoxy derivative (endo)
E(RB3LYP) = -1346.52052381

Zero-point correction= 0.555103 (Hartree/Particle)
Thermal correction to Energy= 0.585282
Thermal correction to Enthalpy= 0.586226
Thermal correction to Gibbs Free Energy= 0.490971
Sum of electronic and ZPE= -1345.965421
Sum of electronic and thermal Energies= -1345.935242
Sum of electronic and thermal Enthalpies= -1345.934297
Sum of electronic and thermal Free Energies= -1346.029553

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	367.270	117.097	200.482

C,0,-0.4639414415,2.4549330261,0.794646555
C,0,-2.1399272574,0.8477593022,-0.0770131507
H,0,-2.2136581982,0.6545119227,-1.1538054447
N,0,-1.807875289,3.0334193082,0.7046884871
C,0,-2.7771832393,2.1992875499,0.2250753304
O,0,-3.9566354325,2.4701143215,0.085407126
N,0,-0.7218497911,1.0713413199,0.2802588735
C,0,-2.114839873,4.4033799769,1.0923467974
H,0,-3.180969714,4.5476567134,0.9116104358
H,0,-1.9075161451,4.5748219188,2.153419786
H,0,-1.5506691271,5.1239938012,0.4919900469
C,0,0.0111309347,2.4268148362,2.2579704072
H,0,0.989450071,1.9504278417,2.3577900108
H,0,0.106857726,3.4474404588,2.6392660032
H,0,-0.7103048379,1.8905086422,2.8814612749
C,0,0.5081164511,3.2159327822,-0.1239843717
H,0,0.6256131947,4.2433618736,0.2319855759
H,0,1.4996081876,2.7590566658,-0.1428679595
H,0,0.1174456375,3.2439644319,-1.1450646474
C,0,0.1895805781,0.1258127334,0.0258903893
C,0,1.5501644664,0.0851094212,0.2911641351
H,0,2.0164191166,0.900703386,0.8264833987
H,0,-0.2348716486,-0.735655195,-0.4890923264
C,0,2.4269867883,-0.8912317435,-0.3666781716
H,0,1.9082027492,-1.4171210595,-1.1687608928
C,0,3.7547110256,-0.3963984574,-0.8816840872
C,0,4.2514372735,-0.9263010413,-2.0873207666
C,0,4.5443735379,0.5446723914,-0.2096765632
C,0,5.4727138945,-0.5259674445,-2.604296788
H,0,3.6635652737,-1.6598039366,-2.6348436659

C,0,5.7773159542,0.9588059019,-0.7140613777
H,0,4.2083794396,0.985258165,0.725562194
C,0,6.2525123234,0.4230253327,-1.9206324344
H,0,5.8476321667,-0.9281124927,-3.5396896152
H,0,6.354154768,1.6951808473,-0.1672491929
O,0,7.4271345022,0.7489014376,-2.5038390988
C,0,-2.8222206719,-0.3199210089,0.7003968218
H,0,-3.3346358679,0.0941425365,1.5770516551
H,0,-2.0344208371,-0.978784448,1.0826817162
C,0,-3.7845070947,-1.1374752678,-0.1408909258
C,0,-4.9473978076,-0.5644844605,-0.6767191294
C,0,-3.5179068751,-2.4885335136,-0.3958234169
C,0,-5.8182082207,-1.3331730491,-1.4492452563
H,0,-5.1612202456,0.4839497488,-0.4903711256
C,0,-4.3911773419,-3.2588017557,-1.1658100604
H,0,-2.6241752623,-2.9502397828,0.0219445131
C,0,-5.5447234348,-2.680550003,-1.6955827835
H,0,-6.7164109796,-0.8777481176,-1.8567563552
H,0,-4.1721217625,-4.3073687804,-1.347732182
H,0,-6.2280127649,-3.2761195217,-2.2941526084
C,0,2.7875014119,-1.5234681831,2.1530028899
H,0,3.2780263248,-0.5529448666,2.2249061698
H,0,3.283613086,-2.194279941,2.8737163621
C,0,1.3224412655,-1.5424960427,2.4387543576
H,0,0.8370631704,-0.9498172189,3.2065545468
C,0,0.7390164407,-2.6035697257,1.7454663127
H,0,-0.2719902085,-2.9698883526,1.8835057003
C,0,2.8155596147,-2.2036895916,0.7810424307
H,0,3.752870697,-2.6202617023,0.4202759712
C,0,1.657491204,-3.0662458638,0.8050710149
H,0,1.4838465783,-3.8786107082,0.1060269493
C,0,8.2730424756,1.7053723518,-1.8695201109
H,0,9.1467609643,1.7991526562,-2.5147623874
H,0,7.7765129093,2.6795776967,-1.7834809956
H,0,8.5876621668,1.3615699766,-0.8766823467

4-methoxy derivative (exo)
E(RB3LYP) = -1346.52183030

Zero-point correction= 0.554580 (Hartree/Particle)
Thermal correction to Energy= 0.584948
Thermal correction to Enthalpy= 0.585892
Thermal correction to Gibbs Free Energy= 0.490338
Sum of electronic and ZPE= -1345.967251

Sum of electronic and thermal Energies= -1345.936882
Sum of electronic and thermal Enthalpies= -1345.935938
Sum of electronic and thermal Free Energies= -1346.031492

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	367.060	117.429	201.110

C,0,-1.1415351009,2.4731004911,0.246078245
C,0,-2.6938802444,0.672395945,-0.4516152492
H,0,-2.6323304564,0.2503404295,-1.4618410368
N,0,-2.463967657,2.9827503867,-0.1290418736
C,0,-3.3638633172,2.0387477135,-0.5336811917
O,0,-4.5160227585,2.2381877233,-0.8760327874
N,0,-1.334471597,1.0052668277,0.0226933167
C,0,-2.8148599101,4.3952607126,-0.0867712183
H,0,-3.8613355201,4.467186384,-0.3867870143
H,0,-2.7037956945,4.8029694925,0.9230954349
H,0,-2.2045021649,4.9805099913,-0.78211053
C,0,-0.8471582685,2.773772995,1.7258900139
H,0,0.0914041388,2.317760131,2.0497779954
H,0,-0.7593773378,3.8529620309,1.8808972741
H,0,-1.6580134949,2.3970304856,2.3563223592
C,0,-0.0657572945,3.0432066072,-0.6952929101
H,0,-0.0024061178,4.1278897672,-0.5702574885
H,0,0.9232839046,2.6297821887,-0.4886161113
H,0,-0.3231407934,2.8275844352,-1.7361341904
C,0,-0.3983286085,0.0486621707,0.0955954033
C,0,0.9224543126,0.1040690771,0.5052403059
H,0,1.3393871532,1.0306109792,0.8764729346
H,0,-0.7648740772,-0.9146262092,-0.2580344971
C,0,1.8265598496,-1.0078528769,0.2550491229
H,0,1.3415452298,-1.7953541339,-0.3265818115
C,0,3.1972304703,-0.7369678751,-0.28714586
C,0,3.7455686416,-1.6281838423,-1.2281631111
C,0,3.974871058,0.3608442387,0.1018477224
C,0,5.0066275777,-1.4257043541,-1.7665796917
H,0,3.1679216836,-2.4911782034,-1.5526469898
C,0,5.2457865409,0.5799915555,-0.4265309497
H,0,3.5976209354,1.0710704131,0.8341471906
C,0,5.7728794235,-0.3163204773,-1.3712659583
H,0,5.4232455717,-2.1097133,-2.4984991275
H,0,5.8140952467,1.443945346,-0.1027709382
O,0,6.9888860974,-0.2035884883,-1.9483390639

C,0,-3.475214132,-0.3161366874,0.469110288
H,0,-4.1345561365,0.2642251576,1.1255914654
H,0,-2.7538924583,-0.8214703504,1.1217014964
C,0,-4.2724312858,-1.3587514954,-0.2912381634
C,0,-5.3004769676,-0.9828256176,-1.1686599115
C,0,-3.987648218,-2.719841539,-0.1265474402
C,0,-6.0205872297,-1.9536642311,-1.8649113945
H,0,-5.5312277107,0.070632626,-1.3018859418
C,0,-4.7116052601,-3.6916520048,-0.8199870232
H,0,-3.2014780013,-3.0271056024,0.5618657499
C,0,-5.7297555236,-3.3091103405,-1.6932997006
H,0,-6.8156456745,-1.6496535041,-2.5400062593
H,0,-4.4818765275,-4.7437614433,-0.6755170111
H,0,-6.2959636157,-4.061920549,-2.2342057396
C,0,2.6474061766,-1.1293937311,2.768937826
H,0,3.7126579079,-0.9421486264,2.8470386965
C,0,1.6537312259,-0.4637170056,3.5049851254
H,0,1.8235788928,0.3387349267,4.2138042532
C,0,0.4202505821,-0.9762726243,3.1400367325
H,0,-0.541692912,-0.6329027288,3.5048971374
C,0,2.0469384573,-1.990504775,1.7973969871
H,0,2.6161033138,-2.8432361835,1.4336665386
C,0,0.6191251589,-2.195548954,2.3046273609
H,0,-0.1469300937,-2.3786032744,1.5494519763
C,0,7.8217761375,0.9006016307,-1.6005091861
H,0,8.7319940609,0.7785384743,-2.1878814644
H,0,7.3454789365,1.8541177691,-1.8586387077
H,0,8.0721810373,0.8888236158,-0.5327788755
H,0,0.6283334377,-3.0721496897,2.9736884664

B3LYP/6-31G* structure for the cycloadduct from the Diels-Alder cycloaddition between cyclopentadiene and *trans*-cinnamaldehyde.

<u>Endo product from parent system</u>
E(RB3LYP) = -1233.26177989

C,0,2.1718360102,1.1023679973,1.3160127959
C,0,0.9104141031,0.5197941584,1.9935949809
C,0,2.5905931395,-0.2362173506,3.3171585449
C,0,3.3337627222,0.5374871883,2.1990861781
H,0,2.253553089,0.8117222815,0.2635842135
H,0,2.1540205281,2.1959352365,1.3480483151
H,0,4.0491120733,-0.0687796634,1.6327681723

H,0,3.9172522626,1.344432486,2.6521040623
C,0,1.3130226307,0.6140889307,3.4794953762
H,0,0.5927046373,0.1902487674,4.1845413258
H,0,1.5368971976,1.639223347,3.7921819192
C,0,0.8866363685,-1.0177733697,1.700601258
H,0,1.2972018249,-1.1780446989,0.6962668453
C,0,1.9339059638,-1.5629524426,2.7853221532
H,0,1.3855419558,-2.0212546888,3.6061914504
H,0,-0.0217451508,1.0105265154,1.7065806406
H,0,3.1836497753,-0.4042112005,4.2202331749
C,0,-0.4553437962,-1.7222440818,1.7388583073
C,0,-0.8540810276,-2.4918182056,0.6358208483
C,0,-1.3303051971,-1.6302099722,2.8339817462
C,0,-2.0839435277,-3.1514808452,0.6222562172
H,0,-0.2010739367,-2.5646477624,-0.2315711005
C,0,-2.5612891426,-2.2875000585,2.8227258119
H,0,-1.0663997705,-1.0304471175,3.700072909
C,0,-2.9416064642,-3.0525713354,1.7182277871
H,0,-2.3732040053,-3.7346746498,-0.2473166006
H,0,-3.2269874336,-2.194511075,3.6760974272
H,0,-3.9014323076,-3.5604301074,1.7096785944
C,0,2.8911500488,-2.5020205555,2.17803565
H,0,3.4827194497,-2.1009159495,1.356304691
C,0,2.5204359538,-4.6305078658,3.509889856
C,0,4.2154703698,-4.4697296361,1.6755425642
C,0,4.097240236,-5.8951670025,2.2013953716
H,0,3.9535692477,-4.4361663201,0.6144634079
N,0,3.1591733295,-3.7406500624,2.4477363759
N,0,3.2104373993,-5.8935388623,3.2450311615
C,0,2.916729035,-7.1193175095,3.979263354
H,0,1.8897565588,-7.4566392941,3.8073194712
H,0,3.6041097611,-7.8787230476,3.6040746741
H,0,3.0814947167,-6.9849313012,5.0524581048
C,0,1.0124511454,-4.7805948469,3.2626648436
H,0,0.4607473215,-3.8550555976,3.4295017456
H,0,0.8205161163,-5.1242367643,2.2424960737
H,0,0.6165455281,-5.5269346885,3.9569859166
C,0,2.8539474569,-4.1029363156,4.9138924905
H,0,2.4773272299,-4.8069627758,5.6609637677
H,0,3.9354703776,-4.007674296,5.0452157364
H,0,2.3827639041,-3.1373955942,5.1102980295
O,0,4.7225573794,-6.8484675245,1.7854927507
C,0,5.636022496,-3.8718825063,1.8918061791
H,0,5.551418119,-2.7785870013,1.8393456901

H,0,5.9706482056,-4.1172410138,2.9059753456
C,0,6.6391305172,-4.3460077411,0.8612406329
C,0,7.4985576376,-5.4182301054,1.1263055664
C,0,6.7178811331,-3.7021468529,-0.3812449531
C,0,8.4188029043,-5.8386770646,0.1661696282
H,0,7.4426455944,-5.9322218781,2.0812423829
C,0,7.6347248604,-4.1230974352,-1.3434832449
H,0,6.0684923118,-2.8542926838,-0.5960614793
C,0,8.4878764562,-5.1941874228,-1.0698190855
H,0,9.0814801899,-6.6707324476,0.3848461993
H,0,7.6897434291,-3.6108977762,-2.2996960884
H,0,9.2062715867,-5.521616346,-1.8155941872

Endo product from *p*-methoxy system

E(RB3LYP) = -1347.78631848

Zero-point correction= 0.583471 (Hartree/Particle)
Thermal correction to Energy= 0.613213
Thermal correction to Enthalpy= 0.614157
Thermal correction to Gibbs Free Energy= 0.520028
Sum of electronic and ZPE= -1347.202847
Sum of electronic and thermal Energies= -1347.173106
Sum of electronic and thermal Enthalpies= -1347.172162
Sum of electronic and thermal Free Energies= -1347.266291

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	384.797	117.083	198.111

C,0,2.3741895581,3.7448731673,-0.0725290096
C,0,3.3495809951,2.5530740376,-0.2069970825
C,0,1.7964713269,2.1184047086,-1.8014072068
C,0,1.2775605862,3.4196753619,-1.1402157582
H,0,1.9700420415,3.8420412298,0.9404255021
H,0,2.8816337583,4.6851311283,-0.3085769313
H,0,0.2722819303,3.3369282263,-0.7131716938
H,0,1.2166727193,4.2048043792,-1.8997125679
C,0,3.3233026134,2.3295183112,-1.7324594459
H,0,3.8990020911,1.4696024368,-2.0858232771
H,0,3.643709233,3.2122727646,-2.2954945218
C,0,2.638068002,1.2868032072,0.3774034458
H,0,2.0183964939,1.6064776813,1.2239560061
C,0,1.6754067122,0.8765591432,-0.8459286072
H,0,2.1035298857,0.0143575444,-1.3536479496

H,0,4.3283808508,2.7198181282,0.2470366039
H,0,1.3764499771,1.9177119602,-2.7908638077
C,0,3.5068498682,0.153964518,0.8786173554
C,0,3.2950155011,-0.3583164367,2.1716856827
C,0,4.5377778662,-0.4178602444,0.1205436099
C,0,4.0684242172,-1.3901254238,2.6834572331
H,0,2.5158698395,0.0717081982,2.7980613381
C,0,5.3292798527,-1.45513876,0.6185185418
H,0,4.755355997,-0.0491476856,-0.8776823431
C,0,5.0977642007,-1.9510458894,1.9094967037
H,0,3.9057528869,-1.7734229033,3.685650827
H,0,6.1231606146,-1.8592937365,0.0013151279
O,0,5.7970334876,-2.9517540664,2.4945349351
C,0,0.3074560667,0.6114486516,-0.3779734825
H,0,-0.1879135715,1.4451610647,0.1174898211
C,0,-0.0650817282,-1.8078285593,-1.0476611199
C,0,-1.8173145818,-0.4496805115,0.1112624507
C,0,-2.24757252,-1.9039918843,-0.0351657911
H,0,-1.7692267284,-0.1756706943,1.1688072295
N,0,-0.4256158649,-0.4563174327,-0.440999871
N,0,-1.2765197739,-2.5681997292,-0.7365206191
C,0,-1.4222260873,-3.9837987591,-1.05602388
H,0,-0.6959018958,-4.5965088672,-0.512825252
H,0,-2.4274445007,-4.2704442841,-0.7441266894
H,0,-1.3160927925,-4.1598790358,-2.1306791737
C,0,1.1507840484,-2.4213295348,-0.3385058139
H,0,2.0730958915,-1.86985518,-0.5236226162
H,0,0.9837220798,-2.4704548978,0.7409613162
H,0,1.2969740019,-3.4389851013,-0.7110759819
C,0,0.1251367618,-1.6708956528,-2.5662721901
H,0,0.2660528499,-2.6635976021,-3.0025123614
H,0,-0.7555558459,-1.2148571185,-3.0272508552
H,0,1.0076637335,-1.077518612,-2.8158533617
O,0,-3.2941637497,-2.3683373622,0.3674742989
C,0,-2.7596736592,0.5276334156,-0.6488873235
H,0,-2.2126258209,1.4659090179,-0.808039068
H,0,-2.9722357461,0.1118248511,-1.6401611107
C,0,-4.0417961785,0.816431864,0.1034756415
C,0,-5.2232517839,0.124430525,-0.1858077291
C,0,-4.0556041009,1.796003431,1.1057797827
C,0,-6.3961957503,0.4070903307,0.5141183093
H,0,-5.2255502383,-0.6436006587,-0.9536089357
C,0,-5.2259854884,2.0773868177,1.8090935171
H,0,-3.1488071255,2.3558919571,1.3312168885

C,0,-6.4000076477,1.3817849562,1.5129133306
H,0,-7.306779713,-0.1357096433,0.2785273441
H,0,-5.224064494,2.8434425355,2.579110021
H,0,-7.3144051991,1.6020054739,2.0559613414
C,0,6.8898744531,-3.5324648185,1.7878313967
H,0,7.3065497849,-4.2861567339,2.4565529112
H,0,6.5553445673,-4.013750445,0.8602491172
H,0,7.6577192409,-2.7840037594,1.5574957986

B3LYP structure of Cyclopentadiene
E(RB3LYP) = -194.101058004

Zero-point correction= 0.092893 (Hartree/Particle)
Thermal correction to Energy= 0.097036
Thermal correction to Enthalpy= 0.097980
Thermal correction to Gibbs Free Energy= 0.066951
Sum of electronic and ZPE= -194.008165
Sum of electronic and thermal Energies= -194.004022
Sum of electronic and thermal Enthalpies= -194.003078
Sum of electronic and thermal Free Energies= -194.034107

	E	CV	S
	KCal/Mol	Cal/Mol-K	Cal/Mol-K
Total	60.891	15.531	65.307

C,0,-0.0048416602,0.0000000001,-0.0034628948
H,0,0.0249008896,-0.0027850253,1.0973069212
H,0,1.0464830549,0.0027850255,-0.3310222791
C,0,-0.763674782,-1.1811550133,-0.5508623208
H,0,-0.4940832206,-2.2140455139,-0.3620818353
C,0,-1.8001534081,-0.7349653659,-1.2898439257
H,0,-2.5280242849,-1.3473729666,-1.8124657394
C,0,-0.7680848972,1.1811550134,-0.5446963007
H,0,-0.5023157959,2.214045514,-0.3505714274
C,0,-1.8023511948,0.7349653659,-1.2867710815
H,0,-2.5321408981,1.3473729665,-1.8067100803

B.10 Gaussrate sample input files

p.dat
*General

```
  TITLE
Alkyl radical methyl cyclopentanol
 ultrafine, sstep 0.005, pm
 END

  ATOMS
    1  C
    2  C
    3  C
    4  C
    5  C
    6  O
    7  C
    8  H
    9  H
   10  H
   11  H
   12  H
   13  H
   14  H
   15  H
   16  H
   17  H
   18  H
END

  NOSUPERMOL

  INPUNIT AU

  MDMOVIE ON

*OPTIMIZATION

  OPTMIN  OHOOK
  OPTTS   OHOOK

*SECOND

  HESSCAL HHOOK

*REACT1
  INITGEO  HOOKS
  SPECIES   NONLINRP
```

```
  GEOM
   1
   2
   3
   4
   5
   6
   7
   8
   9
  10
  11
  12
  13
  14
  15
  16
  17
  18
  END
# end of react1 section

*PROD1
  INITGEO  HOOKS
  SPECIES   NONLINRP
  GEOM
   1
   2
   3
   4
   5
   6
   7
   8
   9
  10
  11
  12
  13
  14
  15
  16
  17
  18
```

```
  END
# end of prod1 section

 *START
  INITGEO  HOOKS
  SPECIES   NONLINRP
  GEOM
   1
   2
   3
   4
   5
   6
   7
   8
   9
  10
  11
  12
  13
  14
  15
  16
  17
  18
  END
# end of start section

*PATH

  SCALEMASS  1.00

  INTMU   3
  SSTEP   0.005
  INH     9

  SRANGE
    SLP  2.25
    SLM  -2.25
  END

# RODS ON
  RPM       pagem
```

```
 SIGN   PRODUCT

 IDIRECT   1

 COORD CART

#  INTDEF
# 54-21 58-21 60-58 60-58-24 24-21-54 21-54-56
# 59-58-24-21 60-56-54-51 61-60-56-54
#  END

 PRPATH
  COORD 1 11
  INTERVAL 1
  XMOL
 END

# EXFIRST
#   EXPROD
#   EXNSTEP 300
#   EXSTEP 0.005
# END

# EXSECOND
#   EXREACT
#   EXNSTEP 300
#   EXSTEP 0.005
# END

 SPECSTOP
  CURVE vag
  POINT savegrid
  PERCENTDOWN 95.
 END

*TUNNEL

 QUAD
  NQE   40
  NQTH  40
 END

  SCT
```

```
*RATE


  FORWARDK

  SIGMAF       1
  CVT
# CUS 2
  PRDELG ON
  PRGIGT ON
#  ICVT ON
# MUVT ON
# MUVTOPT
#     prenergy 4
#     niter 30
# END

  TEMP
    315.15
    298.15
    323.15
    273.15
    173.15
    400.15
    100.15
    250.15
    140.15
  END
```

p.70

```
*GRGENERAL

  GRRESTART
  RSTTOL 0.000001

*GRSTART

  CHARGE       0
  MULTIPLICITY  2

*GRREACT1

  CHARGE       0
  MULTIPLICITY  2
```

```
*GRPROD1

 CHARGE       0
 MULTIPLICITY  2

*GRCOMMON

 GRENER
     #p UB3LYP/6-31G* UNITS=AU FCHK NOSYMM
     scf=tight integral(grid=ultrafinegrid) guess=tcheck
 END

 GRFIRST
     #p UB3LYP/6-31G* FORCE UNITS=AU FCHK NOSYMM
     scf=tight integral(grid=ultrafinegrid) guess=tcheck
 END

 GRSEC
     #p UB3LYP/6-31G* FREQ=NORAMAN UNITS=AU FCHK NOSYMM
     scf=tight integral(grid=ultrafinegrid) guess=tcheck
 END

 GRLINK0
    %chk=g09.chk
    %nproc=8
    %mem=4gb
 END
```

p.71

```
%nproc=8
%mem=4gb
%chk=g09.chk
#p UB3LYP/6-31G* opt fchk NOSYMM
scf=tight integral(grid=ultrafine)

SM Alkyl Radical

0 2
 C    1.756213    0.034995    1.912588
 C    2.302339   -0.569417    0.615745
 C    1.306457   -0.077192   -0.451314
 C   -0.069086   -0.030342    0.256855
 C    0.223606   -0.197271    1.817251
```

O	-0.074479	-1.520620	2.033338
C	-0.631389	0.729806	2.691988
H	1.958566	1.113972	1.954399
H	2.166070	-0.419289	2.821009
H	2.265648	-1.662022	0.685642
H	3.336787	-0.279625	0.402706
H	1.292204	-0.712699	-1.342513
H	1.584632	0.932063	-0.779477
H	-0.741864	-0.827617	-0.072228
H	-0.594520	0.919103	0.109675
H	-0.443712	1.784109	2.458604
H	-1.694854	0.517955	2.540547
H	-0.401845	0.568335	3.751252

p.73

%nproc=8
%mem=4gb
%chk=g09.chk
#p UB3LYP/6-31G* opt fchk NOSYMM
scf=tight integral(grid=ultrafine)

Product

0 2

C	-0.512876	-1.229360	1.894882
C	-0.521163	-1.332757	3.420184
C	-1.456494	-2.437177	3.938957
C	-1.451775	-2.569752	5.424848
C	0.434053	-0.164283	1.350782
O	1.151738	0.492924	2.080839
C	0.435049	0.035990	-0.156928
H	-0.230795	-2.192122	1.439922
H	-1.522404	-1.020568	1.508445
H	-0.815020	-0.367516	3.848583
H	0.500708	-1.517173	3.772989
H	-2.482766	-2.256087	3.583974
H	-1.161702	-3.397248	3.470457
H	-0.557938	-2.341011	5.998183
H	-2.278673	-3.040182	5.947482
H	1.193913	0.771340	-0.431873
H	0.631373	-0.910036	-0.676422
H	-0.548897	0.386126	-0.494301

p.75

```
%nproc=8
%mem=4gb
%chk=g09.chk
#p UB3LYP/6-31G* opt=(ts,calcfc,noeigentest) fchk NOSYMM
scf=tight integral(grid=ultrafine)

ts

0 2
 C    1.838908   -0.510434    2.288518
 C    2.194038    0.149597    0.950772
 C    1.122055   -0.323734   -0.047762
 C   -0.224308   -0.134658    0.595636
 C    0.332672   -0.355095    2.593586
 O   -0.345927   -1.373350    2.897983
 C   -0.096710    0.999236    3.175277
 H    2.424079   -0.088380    3.116580
 H    2.040820   -1.586334    2.247196
 H    3.205881   -0.110107    0.618708
 H    2.158143    1.243573    1.042600
 H    1.280463   -1.382883   -0.282278
 H    1.185979    0.233201   -0.994538
 H   -0.984357   -0.899057    0.466750
 H   -0.620119    0.878839    0.635396
 H    0.381290    1.851855    2.682008
 H   -1.183290    1.106183    3.120011
 H    0.189887    1.020750    4.235078
```

B.11 Program for constructing atomic motion reaction coordinate diagrams

The awk program "progatommotion" below takes as input the output from a Gaussian09 IRC calculation, and is called using the command:
awk –f progatommotion filenameContainingIRCouput

The output contains a list of energies relative to the initial energy and a list of total distances each atom has moved relative to the initial geometry in the IRC. The second program below, progatommotionminus, traces the atomic motion in the opposite direction along the IRC. The IRC calculations going forward and reverse from the transition structure should be done separately to make use of these programs.

Program progatommotion

```
BEGIN {
structureskip=1
```

```
structure=0
numatoms=0
}
/CURRENT STRUCTURE/,/CHANGE IN THE REACTION COORDINATE/ {
if (($1>.5) && ($1<100)) {
  if ($1==1) structure++
  atnum[$1]=$2
  x[structure,$1]=$3;y[structure,$1]=$4;z[structure,$1]=$5
  if ($1>numatoms) numatoms=$1
  }
}
/Done/ {
Energy[structure]=$5
}
#/Delta-x Convergence NOT Met/ {
#structure--
#}
END {
#structure--
for (j=1;j<=numatoms;j++) {
  distmoved[1,j]=0
  }
for (k=2;k<=structure;k+=1) {
  for (j=1;j<=numatoms;j++) {
    distx[k,j]=x[k,j]-x[k-1,j]
    disty[k,j]=y[k,j]-y[k-1,j]
    distz[k,j]=z[k,j]-z[k-1,j]
    distmoved[k,j]=distmoved[k-1,j]+(distx[k,j]^2 + disty[k,j]^2 + distz[k,j]^2)^.5
    }
  }
#  print "structure",k
for (k=1;k<=structure;k++) {
  print (Energy[k]-Energy[1])*627.509
  }
for (j=1;j<=numatoms;j++) {
  print "atom ",j
  if (atnum[j]==6) print "C"
  for (k=1;k<=structure;k++) {
    if (atnum[j]==6) print distmoved[k,j]
    }
#    if (atnum[j]==1) print "H",distmoved[k,j]
#    if (atnum[j]==3) print "Li",distmoved[k,j]
#    if (atnum[j]==5) print "B",distmoved[k,j]
#    if (atnum[j]==6) print "C",distmoved[k,j]
```

```
#     if (atnum[j]==7) print "N",distmoved[k,j]
#     if (atnum[j]==8) print "O",distmoved[k,j]
#     if (atnum[j]==9) print "F",distmoved[k,j]
#     if (atnum[j]==11) print "Na",distmoved[k,j]
#     if (atnum[j]==14) print "Si",distmoved[k,j]
#     if (atnum[j]==15) print "P",distmoved[k,j]
#     if (atnum[j]==16) print "S",distmoved[k,j]
#     if (atnum[j]==17) print "Cl",distmoved[k,j]
   }
}
```

Program progatommotionminus

```
BEGIN {
structureskip=1
structure=0
numatoms=0
}
/CURRENT STRUCTURE/,/CHANGE IN THE REACTION COORDINATE/ {
if (($1>.5) && ($1<100)) {
   if ($1==1) structure++
   atnum[$1]=$2
   x[structure,$1]=$3;y[structure,$1]=$4;z[structure,$1]=$5
   if ($1>numatoms) numatoms=$1
   }
}
/Done/ {
Energy[structure]=$5
}
#/Delta-x Convergence NOT Met/ {
#structure--
#}
END {
#structure--
for (j=1;j<=numatoms;j++) {
   distmoved[1,j]=0
   }
for (k=2;k<=structure;k+=1) {
   for (j=1;j<=numatoms;j++) {
      distx[k,j]=x[k,j]-x[k-1,j]
      disty[k,j]=y[k,j]-y[k-1,j]
      distz[k,j]=z[k,j]-z[k-1,j]
      distmoved[k,j]=distmoved[k-1,j]-(distx[k,j]^2 + disty[k,j]^2 + distz[k,j]^2)^.5
      }
```

```
  }
#  print "structure",k
for (k=structure;k>=1;k--) {
  print (Energy[k]-Energy[1])*627.509
  }
for (j=1;j<=numatoms;j++) {
  print "atom ",j
  if (atnum[j]==6) print "C"
  for (k=structure;k>=1;k--) {
    if (atnum[j]==6) print distmoved[k,j]
    }
#    if (atnum[j]==1) print "H",distmoved[k,j]
#    if (atnum[j]==3) print "Li",distmoved[k,j]
#    if (atnum[j]==5) print "B",distmoved[k,j]
#    if (atnum[j]==6) print "C",distmoved[k,j]
#    if (atnum[j]==7) print "N",distmoved[k,j]
#    if (atnum[j]==8) print "O",distmoved[k,j]
#    if (atnum[j]==9) print "F",distmoved[k,j]
#    if (atnum[j]==11) print "Na",distmoved[k,j]
#    if (atnum[j]==14) print "Si",distmoved[k,j]
#    if (atnum[j]==15) print "P",distmoved[k,j]
#    if (atnum[j]==16) print "S",distmoved[k,j]
#    if (atnum[j]==17) print "Cl",distmoved[k,j]
  }
}
```

B.12 Listing of Dynamics Programs for Program Suite PROGDYN

The master control program for dynamics, in the form of a Unix Shell Script, is called progdyngamess. progdyngamess takes as necessary input files:

freqinHP - This is the standard output from a Gaussian 98, 03, or 09 frequency calculation using freq=hpmodes. For isotopically labeled compounds, use freq=(hpmodes,readisotopes).

progdyn.conf – This is a file giving a variety of configuration options, called on by many of the subprograms. progdyn.conf contains explanations of many of the program options.

progdyngamess takes as optional input files:

isomernumber - A number in file isomernumber provides a start for numbering runs.

detour – A signal file that, by existing, signals the program to do a side calculations

nogo – A signal file that, by existing, signals the program to stop between points

methodfile – A file that contains lines to be added to the end of each g09.com input file, such as lines that call for an NMR calculation.

progdyngamess calls the following programs:

proggenHP - An awk program that starts a trajectory, giving each mode its zero point energy (if a quasiclassical calculation) plus random additional excitations depending on the temperature.

prog1stpoint – Awk program that creates the first Gaussian input file for each run

prog2ndpoint – Awk program that creates the second Gaussian input file for each run. prog2ndpoint also checks the energy of the first point to see if it fits with the desired energy, and aborts the run if it does not by creating appropriate output in file Echeck

progdynb – Creates subsequent Gaussian input files until run is completed, used the awk

proganal – A program to analyze the latest point and see if a run is done. This program must be redone for each new system. Elaborate changes are often programmed into proganal, such as the automatic changing of configuration variables. proganal creates the output to dynfollowfile and NMRlist or NMRlistdis

randgen – A program that generates random numbers between 0 and 1. These are generated all at once and stored in a file for use by proggenHP.

progdyngamess has the following output files:

isomernumber – A running tab of the trajectory number

runpointnumber – A running tab of the point in the trajectory

Echeck – output form where prog2ndpoint checks the energy of the trajectory to see if it fits with the desired energy

geoRecord – A record of all of the geoPlusVel files.

geoPlusVel – Created by proggen, this gives the starting positions, velocities, isotopic masses, excitations of the normal modes, and initial displacements of the normal modes for current run.

g09.com – Created by prog1stpoint, prog2ndpoint, and progdynb, this is the latest input file for Gaussian09 for current run and latest point.

olddynrun and olderdynrun – files containing the last two outputs from Gaussian, for creation of the next point

traj, traj1, traj2, traj3, etc. – files containing the geometries and energies for each trajectory, numbered by the isomernumber, in a format suitable for reading by Molden.

dyn - A record of the Gaussian outputs.

dynfollowfile – A short record of the runs and their results.

NMRlist or NMRlistdis – output of NMR predictions at each point in a trajectory

skipstart - A signal file that, by existing, tells progdyngamess that we are in the middle of a run. For trajectories that are propagated forward and backward in time, skipstart keeps track of whether one is in the forward or reverse part.

diagnostics – optional output that follows which subprograms are running and configuration variables, decided by variable in progdyn.conf

vellist – optional output that list the velocities of each atom, decided by variable in progdyn.conf

A number of files starting with 'temp' are created then later erased.

Progdyngamess is an adapted version for of our previously reported program progdynstarterHP that allow us to run dynamic trajectories using GAMESS. The only

differences are in lines that contain paths to input and output files in progdyngamess, and these are lines that are routinely modified in changing computer systems.
The awk program proganal differed for the current study. An example listing of proganal is given below.
The configuration file named progdyn.conf also differed for the current study. An example listing of progdyn.conf is given below.

Program progdyngamess

```
!/bin/bash
#progdyngamess, version of progdynstaterHP modified to use forces from games
#this still uses a freqinHP files generated by gaussian with high-precision modes from Gaussian output with freq=hpmodes
#December 2011
#
#LIMITATIONS - standard version only handles elements up to bromine, must change program to do higher atomic numbers
#   only handles up to 4000th excited state for modes - this could start to affect the initialization of classical modes or transition vectors at
#    extremely high temperatures
#   The routine that checks whether the actual energy approximately equals the desired energy checks for lines containing "SCF Done" or "EUMP2 =" or " Energy="
#   This should handle ordinary calculations HF, DFT, ONIOM, and MP2 calculatons but the routine in prog2ndpoint would have to be changed for other calcs.
#
#                                   OUTLINE
# A. initilize to know where we are
#    start loop
# B. if no file named "skipstart" then generate a new isomer.  Instructions: Get rid of skipstart to start new isomer.
#    the B loop generates geoPlusVel, adds it to geoRecord, generates and runs first and second points, and sets up for continuous loop
# C. loop over propagation steps
#
#  AAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAA
#origdir, randdir, scratchdir, logfile all may need varied from system to system and assigned here or by program calling this one
export LC_ALL=C
echo $1
scratchdir=$1
origdir=`pwd`
cd $origdir
logfile=ivonnelog
randdir=~/bin
programdir=$WORK/binall
```

```
freqfile=$WORK/binall/freqinHP

rm -f nogo    # assume that if someone is starting a job, they want it to go.
rm -f diagnostics goingwell tempdone # diagnostics contains extra info from previous
runs, other two files are from older versions of progdyn

#### Triple 'while' loop - will have to break multiple times to get out, but advantage is
ability to control starting over
while (true)
do

# As long as there is a file "goingwell" the program will not exit entirely by itself
rm -f $scratchdir/goingwell
while (true)
do
#  BBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBBB
  if (test -f skipstart) then
    echo "skipping start and continuing from previous runs"
  else
#
B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1B1
generate geoPlusVel and first input file
    if [ `cat runpointnumber` = "1" ]; then
      echo "XXXX did not complete first point so new isomer started" >> dynfollowfile
    fi
    if [ `cat runpointnumber` = "2" ]; then
     echo "XXXX did not complete second point so new isomer started" >>
dynfollowfile
    fi
    if [ `cat runpointnumber` = "3" ]; then
      echo "XXXX did not complete third point so new isomer started" >> dynfollowfile
    fi
    $randdir/randgen > temp811
# the next 8 lines would have to be changed to use low-precision modes
    awk '/       1        2        3/,/Harmonic frequencies/ ' $freqfile > temp401
    awk '/Frequencies --/ {print $3;print $4;print $5;print $6;print $7}' temp401 >
tempfreqs
    awk '/Reduced masses/ {print $4;print $5;print $6;print $7;print $8}' temp401 >
tempredmass
    awk '/Force constants/ {print $4;print $5;print $6;print $7;print $8}' temp401 >
tempfrc
    awk '/0/ && ((length($1) < 2) && ($1 < 4)) {print}' temp401 > tempmodes
    awk '/has atomic number/ {print}' $freqfile > tempmasses
```

```
    awk '/Standard orientation:/,/tional const/ {if ($3==0) print}' $freqfile >
tempstangeos
    awk -f $programdir/proggenHP $freqfile > geoPlusVel
    if (test -f isomernumber) then
      cp isomernumber temp533
      awk 'BEGIN {getline;i=$1+1;print i,"----trajectory isomer number----"}' temp533
> isomernumber
      rm temp533
    else
      echo "1 ----trajectory isomer number----" > isomernumber
    fi
    echo 1 > runpointnumber
    rm gamess.inp
    awk -f $programdir/prog1stpoint isomernumber > gamess.inp
#
B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B2B
2B2  if first part successfule then clean up and run the first input file, otherwise die
    if (test -s gamess.inp) then
      rm tempfreqs tempredmass tempfrc tempmodes tempstangeos tempmasses
temp401 temp811
      cat isomernumber >> geoRecord
      cat geoPlusVel >> geoRecord
      rm -f $scratchdir/goingwell
      $programdir/rungms gamess $scratchdir > $scratchdir/gamess.log
      cd $origdir
      grep 'EXECUTION OF GAMESS TERMINATED NORMALLY'
$scratchdir/gamess.log > $scratchdir/goingwell
      if (test -s $scratchdir/goingwell) then
        cat $scratchdir/gamess.log >> dyn
        cp $scratchdir/gamess.log olderdynrun
      else
        cp $scratchdir/gamess.log $origdir/gamess.log
        break
      fi
    else
      break
    fi
#
B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B3B
3B3 if B2 worked then you are here.  create 2nd point, run it, and set up for propagation
loop
    rm gamess.inp
    echo 2 > runpointnumber
    awk -f $programdir/prog2ndpoint $scratchdir/gamess.log > gamess.inp
```

```
# before we decide to run this, check the energy
     awk -f $programdir/proganal $scratchdir/gamess.log >> dynfollowfile
  rm -f $scratchdir/tempdone
     tail -1 dynfollowfile | awk '/XXXX/ {print}' > $scratchdir/tempdone
     if (test  -s $scratchdir/tempdone) then
       rm -f dyn
       rm -f traj
       echo 0 > runpointnumber
       break
     fi
     if (test -s gamess.inp) then
       rm -f $scratchdir/goingwell
       $programdir/rungms gamess $scratchdir > $scratchdir/gamess.log
       cd $origdir
       grep 'EXECUTION OF GAMESS TERMINATED NORMALLY'
$scratchdir/gamess.log > $scratchdir/goingwell
       if (test -s $scratchdir/goingwell) then
         cp $scratchdir/gamess.log olddynrun
         cat $scratchdir/gamess.log >> dyn
         awk -f $programdir/proganal $scratchdir/gamess.log >> dynfollowfile
         awk '/ATOM      ATOMIC                    COORDINATES/,/INTERNUCLEAR
DISTANCES/ {if (($2>.5) && ($2<120)) {print}}' olddynrun > old
         awk '/ATOM      ATOMIC                    COORDINATES/,/INTERNUCLEAR
DISTANCES/ {if (($2>.5) && ($2<120)) {print}}' olderdynrun > older
         echo 3 > runpointnumber
         awk -f $programdir/progdynb olddynrun > gamess.inp
         rm -f old older
       else
         cp $scratchdir/gamess.log $origdir/gamess.log
         break
       fi
     else
       break
     fi
# we've just completed a start, so lets skipstart until instructed otherwise
     echo "forward" > skipstart
   fi
# Reverse trajectories starter routine
   if [ `cat skipstart` = "reverserestart" ]; then
     cd $origdir
     rm gamess.inp
     echo 1 > runpointnumber
     awk -f $programdir/prog1stpoint isomernumber > gamess.inp
     if (test -s gamess.inp) then
```

```
      rm -f $scratchdir/goingwell
      $programdir/rungms gamess $scratchdir > $scratchdir/gamess.log
      cd $origdir
      grep 'EXECUTION OF GAMESS TERMINATED NORMALLY'
$scratchdir/gamess.log > $scratchdir/goingwell
      if (test -s $scratchdir/goingwell) then
        cp $scratchdir/gamess.log olderdynrun
      else
        cp $scratchdir/gamess.log $origdir/gamess.log
        break
      fi
    else
break
    fi
    rm gamess.inp
    echo 2 > runpointnumber
    awk -f $programdir/prog2ndpoint $scratchdir/gamess.log > gamess.inp
    awk -f $programdir/proganal $scratchdir/gamess.log >> dynfollowfile
    rm -f $scratchdir/tempdone
    if (test -s gamess.inp) then
      rm -f $scratchdir/goingwell
      $programdir/rungms gamess $scratchdir > $scratchdir/gamess.log
      cd $origdir
      grep 'EXECUTION OF GAMESS TERMINATED NORMALLY'
$scratchdir/gamess.log > $scratchdir/goingwell
      if (test -s $scratchdir/goingwell) then
        cp $scratchdir/gamess.log olddynrun
        cat $scratchdir/gamess.log >> dyn
        awk -f $programdir/proganal $scratchdir/gamess.log >> dynfollowfile
        awk '/ATOM      ATOMIC                    COORDINATES/,/INTERNUCLEAR
DISTANCES/ {if (($2>.5) && ($2<120)) {print}}' olddynrun > old
        awk '/ATOM      ATOMIC                    COORDINATES/,/INTERNUCLEAR
DISTANCES/ {if (($2>.5) && ($2<120)) {print}}' olderdynrun > older
        echo 3 > runpointnumber
        awk -f $programdir/progdynb olddynrun > gamess.inp
        rm -f old older
      else
        cp $scratchdir/gamess.log $origdir/gamess.log
        break
      fi
    else
      break
    fi
# we've just completed a reversestart, so lets skipstart until instructed otherwise
```

```
    echo "reverse" > skipstart
  fi

#
END_of_B___END_of_B___END_of_B___END_of_B___END_of_B___END_of_B_
__END_of_B___END_of_B___

#
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
CCCCCCCCCCC  propagation loop
  while (true)
  do
#increment runpointnumber
    cp runpointnumber $scratchdir/temp533
    awk 'BEGIN {getline;i=$1+1;print i}' $scratchdir/temp533 > runpointnumber
    rm $scratchdir/temp533
    rm -f $scratchdir/goingwell
    $programdir/rungms gamess $scratchdir > $scratchdir/gamess.log
    cd $origdir
    grep 'EXECUTION OF GAMESS TERMINATED NORMALLY'
$scratchdir/gamess.log > $scratchdir/goingwell
    if (test -s $scratchdir/goingwell) then
      mv olddynrun olderdynrun
      cp $scratchdir/gamess.log olddynrun
      awk '/ATOM      ATOMIC                    COORDINATES/,/INTERNUCLEAR
DISTANCES/ {if (($2>.5) && ($2<120)) {print}}' olddynrun > old
      awk '/ATOM      ATOMIC                    COORDINATES/,/INTERNUCLEAR
DISTANCES/ {if (($2>.5) && ($2<120)) {print}}' olderdynrun > older
      awk -f $programdir/progdynb olddynrun > gamess.inp
      rm -f old older
    else
      cp $scratchdir/gamess.log $origdir/gamess.log
      break
    fi

#stop it all nicely by creating a nogo file
    if (test  -f nogo) then
      break
    fi

#figure out if this isomer is done
    awk -f $programdir/proganal $scratchdir/gamess.log >> dynfollowfile
    rm -f $scratchdir/tempdone
    tail -2 dynfollowfile | awk '/XXXX/ {print}' > $scratchdir/tempdone
```

```
    if (test  -s $scratchdir/tempdone) then
      if [ `awk '/reversetraj/ {if ($1=="reversetraj") print $2}' progdyn.conf` = "true" ];
then
        if [ `cat skipstart` = "reverse" ]; then
          rm -f skipstart
          rm -f geoPlusVel
          rm -f olddynrun
          rm -f olderdynrun
          a=`awk '{print $1}' isomernumber`
          mv traj traj$a
          mv dyn dyn$a
        fi
        if [ `cat skipstart` = "forward" ]; then
          echo reverserestart > skipstart
        fi
      else
        rm -f skipstart
        rm -f geoPlusVel
        rm -f olddynrun
        rm -f olderdynrun
        a=`awk '{print $1}' isomernumber`
        mv traj traj$a
        mv dyn dyn$a
      fi
      break
    fi
  done
#
END_of_C_Loop____END_of_C_Loop____END_of_C_Loop____END_of_C_Loop__
__END_of_C_Loop____END_of_C_Loop____

# We've got to break a second time to get out of this loop
# if we really want to quit.  Otherwise, it will start over
# at the top
  if (test  -f nogo) then
    break
  fi
  if (test  -s $scratchdir/goingwell) then
    echo "starting a new point or a new direction"
  else
    break
  fi
done
```

```
  if (test  -f nogo) then
    break
  fi
  if (test  -s $scratchdir/goingwell) then
    echo "starting a new point or a new direction2"
  else
    break
  fi
done
exit 0
```

Program proggenHP

```
BEGIN {
# Aut 2010 changes classicalSpacing to 2 and upped possible excited states to 4000
# Jan 2009 - a number of little changes to improve reporting, precision, etc, specification of displacement on particular modes
# Jan 2009 cannonball trajectories.  adds desired energy to initial velocities based on file cannontraj, so one can shoot toward a ts
# updated Nov 2008 to incorporate running DRPs
# updated Nov 2008 to allow for start without an initial freq calc using classical = 2
# updated Aug 2008 added to atom list to handle a large number of atoms without changes needed
# updated June 2008 to incorportate new method for choosing displacements with initialdis 2
# updated Jan 17 2008 - bug fix for > 99 atoms, 300 excitations of low modes possible
# version August 2007 - incorporates classical trajectory calculation option
#also allows listing of number of imaginary frequencies
# version Sept 16, 2005 - incorportates searchdir but not yet rotation
# now reads random numbers from temp811, starting at a random place
# The input files are generated before this and are tempfreqs, tempredmass,
# tempfrc, tempmodes, and tempstangeos.
# It will count the number of atoms.

# default parameters, including quassiclassical, no displacements, transition state, not a DRP
# do not change these - rather, change progdyn.conf to set the parameters
initialDis=0; timestep=1E-15; scaling=1.0; temp=298.15
classical=0; numimag=1; DRP=0; cannonball=0
charge=0; multiplicity=1; method="HF/3-21G"; memory=20000000
diag=1; checkpoint="g09.chk"; searchdir="positive"; boxon=0
boxsize=10; maxAtomMove=0.1; title1="you"; title2="need"
title3="a"; title4="progdyn.conf"; processors=1; highlevel=999
conver1=4.184E26 #dividing by this converts amu angs^2 /s^2 to kcal/mol
geometry="nonlinear"
```

```
#initialization and constants
for (i=1;i<=10000;i++) {disMode[i]=-1}
i=1;j=1;k=1
c=29979245800; h=6.626075E-34; avNum=6.0221415E23
RgasK=0.00198588; RgasJ=8.31447
numAtoms=0; atomnumber=0; classicalSpacing=2
zpeGauss=0; zpeGaussK=0; zpePlusE=0; potentialE=0

# read progdyn.conf for configuration info
blankLineTester=10
while (blankLineTester>1) {
  getline < "progdyn.conf"
  if ($1=="method") method=$2
  if ($1=="charge") charge=$2
  if ($1=="multiplicity") multiplicity=$2
  if ($1=="memory") memory=$2
  if ($1=="processors") processors=$2
  if ($1=="checkpoint") checkpoint=$2
  if ($1=="diagnostics") diag=$2
  if ($1=="initialdis") initialDis=$2
  if ($1=="timestep") timestep=$2
  if ($1=="scaling") scaling=$2

if ($1=="temperature") temp=$2
  if ($1=="searchdir") searchdir=$2
  if ($1=="classical") classical=$2
  if ($1=="numimag") numimag=$2
  if ($1=="geometry") geometry=$2
  if ($1=="highlevel") highlevel=$2
  if ($1=="boxon") boxon=$2
  if ($1=="boxsize") boxsize=$2
  if ($1=="DRP") DRP=$2; if (DRP==1) classical=2 #this lets one start a DRP from a
point that is not a freq calc
  if ($1=="maxAtomMove") maxAtomMove=$2
  if ($1=="cannonball") cannonball=$2
  if ($1=="displacements") disMode[$2]=$3
  if ($1=="controlphase") controlPhase[$2]=$3
  if ($1=="title") {
    title1=$2
    title2=$3
    title3=$4
    title4=$5
    }
```

```
  blankLineTester=length($0)
  }

if (diag>=1) print "***************** starting proggen *****************" >>
"diagnostics"
if (diag>=1) print "method,charge,multiplicity,memory" >> "diagnostics"
if (diag>=1) print method,charge,multiplicity,memory >> "diagnostics"
if (diag>=1) print "processors,checkpoint,title,initialdis,timestep,scaling,temperature" >>
"diagnostics"
if (diag>=1) print
processors,checkpoint,title1,title2,title3,title4,initialDis,timestep,scaling,temp >>
"diagnostics"
if (diag>=1) print
"classical,numimag,highlevel,boxon,boxsize,DRP,maxAtomMove,cannonball" >>
"diagnostics"
if (diag>=1) print
classical,numimag,highlevel,boxon,boxsize,DRP,maxAtomMove,cannonball >>
"diagnostics"

# put geometries into array, also figure out number of atoms
# note that this picks out the last geometry in a file, assuming
# that if there is an optimization followed by a freq, nothing else follows
# kludgy - repeats last line twice - must be a better way
do {
  getline < "tempstangeos"
  if (oldline==$0) $0=""
  oldline=$0
  atom = $1
  if (atom>numAtoms) numAtoms=atom
  atNum[atom]=$2
  geoArr[atom,1]=$4; geoArr[atom,2]=$5; geoArr[atom,3]=$6
  velArr[atom,1]=0; velArr[atom,2]=0; velArr[atom,3]=0
  }
while (length($0) > 0)

#output the number of atoms, used in many routines
print numAtoms

# put in atomic symbols and atomic weights - assigns a default mass but then reads it
from tempmasses when possible
for (i=1;i<=numAtoms;i++) {
  getline < "tempmasses"
  if (atNum[i]==1) {atSym[i]="H";atWeight[i]=1.00783}
  if (atNum[i]==2) {atSym[i]="He";atWeight[i]=4.0026}
```

```
   if (atNum[i]==3) {atSym[i]="Li";atWeight[i]=6.941}
   if (atNum[i]==4) {atSym[i]="Be";atWeight[i]=9.012}
   if (atNum[i]==5) {atSym[i]="B";atWeight[i]=10.811}
   if (atNum[i]==6) {atSym[i]="C";atWeight[i]=12.}
   if (atNum[i]==7) {atSym[i]="N";atWeight[i]=14.007}
   if (atNum[i]==8) {atSym[i]="O";atWeight[i]=15.9994}
   if (atNum[i]==9) {atSym[i]="F";atWeight[i]=18.9984}
   if (atNum[i]==10) {atSym[i]="Ne";atWeight[i]=20.1797}
   if (atNum[i]==11) {atSym[i]="Na";atWeight[i]=22.989}
   if (atNum[i]==12) {atSym[i]="Mg";atWeight[i]=24.305}
   if (atNum[i]==13) {atSym[i]="Al";atWeight[i]=26.98154}
   if (atNum[i]==14) {atSym[i]="Si";atWeight[i]=28.0855}
   if (atNum[i]==15) {atSym[i]="P";atWeight[i]=30.9738}
   if (atNum[i]==16) {atSym[i]="S";atWeight[i]=32.066}
   if (atNum[i]==17) {atSym[i]="Cl";atWeight[i]=35.4527}
   if (atNum[i]==18) {atSym[i]="Ar";atWeight[i]=39.948}
   if (atNum[i]==19) {atSym[i]="K";atWeight[i]=39.0983}
   if (atNum[i]==20) {atSym[i]="Ca";atWeight[i]=40.078}
   if (atNum[i]==21) {atSym[i]="Sc";atWeight[i]=44.96}
   if (atNum[i]==22) {atSym[i]="Ti";atWeight[i]=47.867}
   if (atNum[i]==23) {atSym[i]="V";atWeight[i]=50.94}
   if (atNum[i]==24) {atSym[i]="Cr";atWeight[i]=51.9961}
   if (atNum[i]==25) {atSym[i]="Mn";atWeight[i]=54.938}
   if (atNum[i]==26) {atSym[i]="Fe";atWeight[i]=55.845}
   if (atNum[i]==27) {atSym[i]="Co";atWeight[i]=58.933}
   if (atNum[i]==28) {atSym[i]="Ni";atWeight[i]=58.693}
   if (atNum[i]==29) {atSym[i]="Cu";atWeight[i]=63.546}
if (atNum[i]==30) {atSym[i]="Zn";atWeight[i]=65.38}
   if (atNum[i]==31) {atSym[i]="Ga";atWeight[i]=69.723}
   if (atNum[i]==32) {atSym[i]="Ge";atWeight[i]=72.64}
   if (atNum[i]==33) {atSym[i]="As";atWeight[i]=74.9216}
   if (atNum[i]==34) {atSym[i]="Se";atWeight[i]=78.96}
   if (atNum[i]==35) {atSym[i]="Br";atWeight[i]=79.904}
   if (atNum[i]==46) {atSym[i]="Pd";atWeight[i]=106.42}
   if (atNum[i]==53) {atSym[i]="I";atWeight[i]=126.90447}
# gets actual weight from freqinHP when possible so a prior calc with readisotopes gets
you isotopic substitution
   if ((i<100) && ($9>0)) atWeight[i]=$9
   if ((i>99) && ($8>0)) atWeight[i]=$8

   if ((diag>1) && (i==1)) print
"atNum[i],atSym[i],atWeight[i],geoArr[i,1],geoArr[i,2],geoArr[i,3]" >> "diagnostics"
   if (diag>1) print atNum[i],atSym[i],atWeight[i],geoArr[i,1],geoArr[i,2],geoArr[i,3] >>
"diagnostics"
```

```
  }

# read in frequencies, scale them, read in Reduced masses, read in force
#constants, replace negative frequencies by 2 wavenumbers
numFreq=3*numAtoms-6
if (geometry=="linear") numFreq=3*numAtoms-5
for (i=1;i<=numFreq;i++) {
  $0=""
  getline < "tempfreqs"
  freq[i]=$0*scaling
  if (freq[i]<0) freq[i]=2
  }
for (i=1;i<=numFreq;i++) {
  $0=""
  getline < "tempredmass"
  redMass[i]=$0
  if (redMass[i]=="") redMass[i]=1.
  }
for (i=1;i<=numFreq;i++) {
  $0=""
  getline < "tempfrc"
  frc[i]=$0
  if (frc[i]=="") frc[i]=0.0001
  if (frc[i]==0) frc[i]=0.0001
  if ((diag>1) && (i==1)) print "freq[i],redMass[i],frc[i]" >> "diagnostics"
  if (diag>1) print freq[i],redMass[i],frc[i] >> "diagnostics"
  }

# read in the modes - note that trajectories always need a freq calc with freq=hpmodes
unless classical=2
if (classical!=2) {
  for (i=1;i<=numFreq;i+=5) {
    for (j=1;j<=(3*numAtoms);j++) {
      getline < "tempmodes"
      mode[i,$2,$1]=$4; mode[i+1,$2,$1]=$5; mode[i+2,$2,$1]=$6;
mode[i+3,$2,$1]=$7; mode[i+4,$2,$1]=$8
      }
    }
  }
if (diag>2) {for (i=1;i<=numFreq;i++) {print mode[i,1,1],mode[i,1,2],mode[i,1,3] >>
"modesread"}}

# if doing a cannonball trajectory, read in the vector
if (cannonball>0) {
```

```
  for (i=1;i<=numAtoms;i++) {
    getline < "cannontraj"
    cannonArr[i,1]=$1; cannonArr[i,2]=$2; cannonArr[i,3]=$3
    }
  }

# collect a series of random numbers from file temp811, generated from an outside
random number generator called by prodynstarterHP
# read from temp811, starting at a random place
srand(PROCINFO["pid"]); tester=rand()*1000
for (i=1;i<=tester;i++) getline < "temp811"
for (i=1;i<=numFreq;i++) {
  getline < "temp811"; randArr[i]=$1
getline < "temp811"; randArrB[i]=$1
  getline < "temp811"; randArrC[i]=$1
}
# for a QM distribution for a harmonic oscillator in its ground state, we want to generate
a set of random numbers
#between -1 and 1 weighted such that numbers toward the center are properly more
common
i=1
while (i<=numFreq) {
  if ((initialDis==2) || (disMode[i]==2)) {
    getline < "temp811"
    tempNum=2*($1-.5)
    prob=exp(-(tempNum^2))
    getline < "temp811"
    if ($1<prob) {
      randArrD[i]=tempNum
      i++
      }
    }
  if ((initialDis!=2) && (disMode[i]!=2)) i++
  }

# to start without normal modes or frequencies we need to just pick a random direction
for the motion of each atom, requiring 3N random numbers
for (i=1;i<=numAtoms;i++) {
  for (j=1;j<=3;j++) {
  getline < "temp811"
  if ($1>0.5) randArrE[i,j]=1
  if ($1<.5) randArrE[i,j]=-1
    }
  }
```

```
# determine energy in each normal mode
for (i=1;i<=numFreq;i++) {
  zpeJ[i]=0.5*h*c*freq[i]       #units J per molecule
#if classical, treat as modes spaced by classicalSpacing wavenumbers
  if (classical==1) zpeJ[i]=0.5*h*c*classicalSpacing  # the zpe is not used when
classical but the spacing is used to calculate the E in mode
  zpeK[i]=zpeJ[i]*avNum/4184    #units kcal/mol
  if (temp<10) vibN[i]=0        # avoids working with very small temperatures - if the
temp is too low, it just acts like 0 K
  if (temp>=10) {
    zpeRat[i]=exp((-2*zpeK[i])/(RgasK*temp))
    if (zpeRat[i]==1) zpeRat[i]=.99999999999
    Q[i]=1/(1-zpeRat[i])
    newRand=randArr[i]
    vibN[i]=0
    tester=1/Q[i]
#     get up to 4000 excitations of low modes
    for (j=1;j<=(4000*zpeRat[i]+2);j++) {
      if (newRand>tester) vibN[i]++
      tester=tester+((zpeRat[i]^j)/Q[i])
      }
    }
  }
# figure out mode energies and maximum classical shift and then actual shift
# also calculated total energy desired for molecule
desiredModeEnK=0
for (i=1;i<=numFreq;i++) {
  modeEn[i]=(zpeJ[i]*1E18)*(2*vibN[i]+1) # units here are mDyne Ansgroms for
compatability with Gaussian force constants
  if (classical==1) modeEn[i]=(zpeJ[i]*1E18)*2*vibN[i]    #no zpe when classical
  modeEnK[i]=zpeK[i]*(2*vibN[i]+1)
  if (classical==1) modeEnK[i]=zpeK[i]*2*vibN[i]          #no zpe when classical
  desiredModeEnK=desiredModeEnK + modeEnK[i]
# no 1/2 hv for imaginary frequencies
# treating modes with frequencies <10 as translations, ignoring their zero point energies
  if (freq[i]<10) modeEn[i]=(zpeJ[i]*1E18)*(2*vibN[i])
  maxShift[i]=(2*modeEn[i]/frc[i])^0.5
  if (initialDis==2) shift[i]=maxShift[i]*randArrD[i]
  if (initialDis==1) shift[i]=maxShift[i]*(2*(randArrC[i]-0.5))
  if (initialDis==0) shift[i]=0
# lines below allow for setting of displacement mode for individual modes
# It used to be necessary to use disMode 10 to turn off displacements for a mode, but
hopefully that bug is killed and you can use disMode 0
```

```
  if (disMode[i]==2) shift[i]=maxShift[i]*randArrD[i]
  if (disMode[i]==1) shift[i]=maxShift[i]*(2*(randArrC[i]-0.5))
  if (disMode[i]==10) shift[i]=0 #kept for backward compatability
  if (disMode[i]==0) shift[i]=0
# no displacements along imaginary frequencies and very low ones - it is better to treat
these
# as translations - employing a shift can give you initial weird geometries
  if (freq[i]<10) shift[i]=0
  if (numimag==1) shift[1]=0
  if (numimag==2) shift[2]=0
  }
for (i=1;i<=numFreq;i++) {
  if ((diag>1) && (i==1)) print
"zpeJ[i],zpeK[i],zpeRat[i],Q[i],vibN[i],modeEn[i],maxShift[i],shift[i]" >> "diagnostics"
  if (diag>1) print zpeJ[i],zpeK[i],zpeRat[i],Q[i],vibN[i],modeEn[i],maxShift[i],shift[i]
>> "diagnostics"
  }

# multiply each of the modes by its shift and add them up
# Do not do this if classical=2
if (classical!=2) {
  for (i=1;i<=numFreq;i++) {
    for (j=1;j<=numAtoms;j++) {
      for (k=1;k<=3;k++) {
        shiftMode[i,j,k]=mode[i,j,k]*shift[i]
        geoArr[j,k]=geoArr[j,k]+shiftMode[i,j,k]
        }
      }
    }
  }
#now start toward velocities
for (i=1;i<=numFreq;i++) {
  kinEn[i]=100000*(modeEn[i]-0.5*frc[i]*shift[i]^2)  # the 100000 converts to g
angstrom^2 s^2
  vel[i]=(2*kinEn[i]/(redMass[i]/avNum))^0.5        # in angstrom / s
#use searchdir in progdyn.conf to control the direction for trajectories started from a
saddle point
  if (numimag>1) numimag=1  #only the first freq can be sent in the searchdir direction,
the rest go in a random direction
  if (i>numimag) {
    if (randArrB[i]<0.5) vel[i]=-vel[i]
    }
  if (i==numimag) {
    if (searchdir=="negative") vel[i]=-vel[i]
```

```
    }
  if ((diag>1) && (i==1)) print "vel[i]" >> "diagnostics"
  if (diag>1) print vel[i] >> "diagnostics"
  }

# if controlphase is being used, set the velocity on particular modes as positive or
negative as requested
for (i=1;i<=numFreq;i++) {
  if ((controlPhase[i]=="positive") && (vel[i]<0)) vel[i]=-vel[i]
  if ((controlPhase[i]=="negative") && (vel[i]>0)) vel[i]=-vel[i]
  }

# multiply each of the modes by its velocity and add them up
# Do not do this if classical=2
if (classical!=2) {
  for (i=1;i<=numFreq;i++) {
    for (j=1;j<=numAtoms;j++) {
      for (k=1;k<=3;k++) {
        velMode[i,j,k]=mode[i,j,k]*vel[i]*timestep
        velArr[j,k]=velArr[j,k]+velMode[i,j,k]
        }
      }
    }
  }

# to start without normal modes or frequencies we figure out the energy per atom based
on 1/2RT in degree of freedom
if (classical==2) {
  degFreedomEnK=temp*RgasK
  degFreedomEnJ=degFreedomEnK/(avNum/4184)
  cartEn=degFreedomEnJ*1E18
  kinEnCart=100000*cartEn
#print degFreedomEnK, degFreedomEnJ, cartEn, kinEnCart
  for (i=1;i<=numAtoms;i++) {
    for (j=1;j<=3;j++) {
      velArr[i,j]=randArrE[i,j]*timestep*(2*kinEnCart/(atWeight[i]/avNum))^0.5
      if (DRP==1) velArr[i,j]=0
      }
    }
}


# calculate the KE in the modes at this point
KEinitmodes=0
```

```
for (j=1;j<=numAtoms;j++) {
  KEinitmodes=KEinitmodes + 0.5*atWeight[j]*(velArr[j,1]^2 + velArr[j,2]^2 +
velArr[j,3]^2)/((timestep^2)*conver1)
  }

# if doing a cannonball, adjust multiplier until extra energy is correct
if (cannonball>0) {
  multiplier=1; tester=0; tolerance=.1
  while (tester==0) {
    KEinittotal=0
    for (j=1;j<=numAtoms;j++) {
      cannonvelArr[j,1]=velArr[j,1]+multiplier*cannonArr[j,1];
cannonvelArr[j,2]=velArr[j,2]+multiplier*cannonArr[j,2];
cannonvelArr[j,3]=velArr[j,3]+multiplier*cannonArr[j,3]
      KEinittotal=KEinittotal + 0.5*atWeight[j]*(cannonvelArr[j,1]^2 +
cannonvelArr[j,2]^2 + cannonvelArr[j,3]^2)/((timestep^2)*conver1)
      }
    if (KEinittotal>(KEinitmodes+cannonball+tolerance))
multiplier=multiplier*0.98901364
    if (KEinittotal<(KEinitmodes+cannonball-tolerance)) multiplier=multiplier*1.01
    if ((KEinittotal<(KEinitmodes+cannonball+tolerance)) &&
(KEinittotal>(KEinitmodes+cannonball-tolerance))) tester=1
    }
  for (j=1;j<=numAtoms;j++) {
    velArr[j,1]=velArr[j,1]+multiplier*cannonArr[j,1];
velArr[j,2]=velArr[j,2]+multiplier*cannonArr[j,2];
velArr[j,3]=velArr[j,3]+multiplier*cannonArr[j,3]
    }
  }

#output the new geometry.
# ****** this section changed for special experiment for cyclopentadiene.  do not use
this for other cases
# atWeight[4]=140.0001
# ****** line below added for special experiment switching mass from 12 to 140,
keeping momenta the same
#velArr[4,1]=velArr[4,1]/11.66667; velArr[4,2]=velArr[4,2]/11.66667;
velArr[4,3]=velArr[4,3]/11.66667
for (j=1;j<=numAtoms;j++) {
  printf("%2s % .7f % .7f % .7f %9.5f
\n",atSym[j],geoArr[j,1],geoArr[j,2],geoArr[j,3],atWeight[j])
  }

#output the velocities and calculate the total kinetic energy overall
```

```
KEinittotal=0
for (j=1;j<=numAtoms;j++) {
  KEinittotal=KEinittotal + 0.5*atWeight[j]*(velArr[j,1]^2 + velArr[j,2]^2 +
velArr[j,3]^2)/((timestep^2)*conver1)
  printf("% .8f % .8f % .8f \n",velArr[j,1],velArr[j,2],velArr[j,3])
  }

#anything else I add to the file will not affect the trajectories but will keep a record and
be good for analysis
for (i=1;i<=numFreq;i++) {
  if (initialDis==0) printf("%.6f   % .6f    %4i    % 1.4e       % .6f %1i\n", randArr[i],
randArrB[i], vibN[i], vel[i], shift[i], disMode[i])
  if (initialDis==1) printf("%.6f   % .6f    %4i    % 1.4e       % .6f %1i\n", randArr[i],
randArrC[i], vibN[i], vel[i], shift[i], disMode[i])
  if (initialDis==2) printf("%.6f   % .6f    %4i    % 1.4e       % .6f %1i\n", randArr[i],
randArrD[i], vibN[i], vel[i], shift[i], disMode[i])
  }
print "temp ",temp
print "initialDis",initialDis
print "classical",classical
print "timestep",timestep
print "numimag",numimag
OFMT = "%.3f"
print "Total mode energy desired=",desiredModeEnK
print "KE initial from modes=",KEinitmodes,"   KE initial total=",KEinittotal
if (cannonball>0) print "cannonball",cannonball,"  cannon Energy=",KEinittotal-
KEinitmodes
if (boxon>0) print "boxsize",boxsize
if (DRP>0) print "DRP",DRP,"   maxAtomMove",maxAtomMove
if (DRP>0) print maxAtomMove > "maxMove"
}  # End of BEGIN

/Zero-point correction/ {zpeGauss=$3}
/zero-point Energies/ {zpePlusE=$7}
END {
zpeGaussK=zpeGauss*627.509
potentialE=zpePlusE - zpeGauss
OFMT = "%.6f"
print "Gaussian zpe=",zpeGauss,"or",zpeGaussK,"kcal/mol  E + zpe=",zpePlusE,"
potential E=",potentialE
print "" #will use blank line to mark end of geoPlusVel file
}
```

Program prog1stpoint

```
BEGIN {
# aug 2010 changed so that it is more careful in reading in from geoPlusVel
#     removed some default parameters that should always be defined
# Jan 2009 - a number of little changes to improve reporting, precision, etc
# aug 2008 added to atom list so handles H to Cl without change needed
# version Feb 2008 incorporates methodfile, boxon and boxsize, though this point
unaffected by box
# version Jan 2008 - allows for ONIOM jobs, fixed atoms
# version Sept 2005 - incorportates meth3, meth4, meth5, meth6, but not yet rotation
# this program creates the first input file for g09
# the title should be changed as appropriate
# the isomer number comes from a file isomernumber

# default parameters, including quassiclassical, no displacements, transition state, not a
DRP
# do not change these - rather, change progdyn.conf to set the parameters
initialDis=0; timestep=1E-15; scaling=1.0; temp=298.15
classical=0; numimag=1; DRP=0; cannonball=0
memory=20000000
diag=1; checkpoint="g09.chk"; searchdir="positive"; boxon=0
boxsize=10; maxAtomMove=0.1; title1="you"; title2="need"
title3="a"; title4="progdyn.conf"; processors=1; highlevel=999; linkatoms=0
geometry="nonlinear"

#initialization
i=1;j=1;k=1
c=29979245800; h=6.626075E-34; avNum=6.0221415E23
RgasK=0.00198588; RgasJ=8.31447
numAtoms=0; atomnumber=0

# read progdyn.conf for configuration info
blankLineTester=10
while (blankLineTester>1) {
  getline < "progdyn.conf"
  if ($1=="method") method=$2
  if ($1=="method2") meth2=$2
  if ($1=="charge") charge=$2
  if ($1=="multiplicity") multiplicity=$2
  if ($1=="memory") memory=$2
  if ($1=="processors") processors=$2
  if ($1=="checkpoint") checkpoint=$2
  if ($1=="timestep") timestep=$2
  if ($1=="diagnostics") diag=$2
  if ($1=="method3") meth3=$2
```

```
  if ($1=="method4") meth4=$2
  if ($1=="method5") meth5=$2
  if ($1=="method6") meth6=$2
  if ($1=="highlevel") highlevel=$2
  if ($1=="linkatoms") linkatoms=$2
  if ($1=="fixedatom1") fixedatom1=$2
  if ($1=="fixedatom2") fixedatom2=$2
  if ($1=="fixedatom3") fixedatom3=$2
if ($1=="fixedatom4") fixedatom4=$2
  if ($1=="methodfile") methodfilelines=$2
  if ($1=="killcheck") killcheck=$2
  if ($1=="title") {
    title1=$2
    title2=$3
    title3=$4
    title4=$5
    }
  blankLineTester=length($0)
  }

if (diag==1) print "***************** starting prog1stpoint *****************" >>
"diagnostics"
if (diag==1) print "method,charge,multiplicity,memory" >> "diagnostics"
if (diag==1) print method,charge,multiplicity,memory >> "diagnostics"
if (diag==1) print "processors,checkpoint,title" >> "diagnostics"
if (diag==1) print processors,checkpoint,title1,title2,title3,title4 >> "diagnostics"

getline < "isomernumber"
isomernum = $1
#read in number of atoms, geometry, masses, and velocity from geoPlusVel
getline < "geoPlusVel"
numAtoms=$1
# geometry
for (i=1;i<=numAtoms;i++) {
  getline < "geoPlusVel"
  weight[i]=$5
  atSym[i]=$1
  if (atSym[i]=="H") atNum[i]=1.0
  if (atSym[i]=="Li") atNum[i]=3.0
  if (atSym[i]=="B") atNum[i]=5.0
  if (atSym[i]=="C") atNum[i]=6.0
  if (atSym[i]=="N") atNum[i]=7.0
  if (atSym[i]=="O") atNum[i]=8.0
  if (atSym[i]=="F") atNum[i]=9.0
```

```
  if (atSym[i]=="Na") atNum[i]=11.0
  for (j=1;j<=3;j++) {
    geoArr[i,j]=$(1+j)
    }
  }
#velocities not needed for 1st point
for (i=1;i<=numAtoms;i++) {
  getline < "geoPlusVel"
  for (j=1;j<=3;j++) {
    velArr[i,j]=$j
    }
  }

# TO DO: rather than putting in the details here, the program should get the details from
progdyn.conf
# and progdyn.conf should have control over #proc, memory, method, basis set, etc
# though this will work for now
print " $CONTRL DFTTYP=B3PW91 RUNTYP=Gradient COORD=UNIQUE
NZVAR=0 $END"
print " $SYSTEM MWORDS=196 TIMLIM=30 $END"
print " $BASIS  GBASIS=N31 NGAUSS=6 NDFUNC=1 $END"
print " $INTGRL NINTIC=-150000000 $END"
print " $DFT NRAD=75 NLEB=302 $END"
print " $GUESS  GUESS=HUCKEL $END"
print " $DATA"
print title1,title2,title3,title4,"runpoint 1","runisomer ",isomernum
print "C1"
}

END {
for (i=1;i<=numAtoms;i++) {
  printf("%s %.2f %.7f %.7f
%.7f",atSym[i],atNum[i],geoArr[i,1],geoArr[i,2],geoArr[i,3])
  print ""
  }
print " $END"
}
```

Program prog2ndpoint

```
BEGIN {
#Aug 2010 added etolerance to make it controllable from progdyn.conf, made it so that
DRP does not check energy
# aug 2008 added to atom list so handles 1 to 17 without change needed
```

```
# version Feb 2008 incorporates methodfile, boxon and boxsize, though this point
unaffected by box
# version Jan 2008 - allows for ONIOM jobs, fixed atoms
# version Sept 9, 2005 - incorportates meth3, meth4, meth5, meth6, but not yet rotation
# read progdyn.conf for configuration info

# default parameters, including quassiclassical, no displacements, transition state, not a
DRP
# do not change these - rather, change progdyn.conf to set the parameters
initialDis=0; timestep=1E-15; scaling=1.0; temp=298.15
classical=0; numimag=1; DRP=0; cannonball=0
memory=20000000
diag=1; checkpoint="g09.chk"; searchdir="positive"; boxon=0
boxsize=10; maxAtomMove=0.1; title1="you"; title2="need"
title3="a"; title4="progdyn.conf"; processors=1; highlevel=999; linkatoms=0
etolerance=1

#initialization
i=1;j=1;k=1
c=29979245800; h=6.626075E-34; avNum=6.0221415E23
RgasK=0.00198588; RgasJ=8.31447
numAtoms=0; atomnumber=0

blankLineTester=10
while (blankLineTester>1) {
  getline < "progdyn.conf"
  if ($1=="method") method=$2
  if ($1=="method2") meth2=$2
  if ($1=="charge") charge=$2
  if ($1=="multiplicity") multiplicity=$2
  if ($1=="memory") memory=$2
  if ($1=="processors") processors=$2
  if ($1=="checkpoint") checkpoint=$2
  if ($1=="timestep") timestep=$2
  if ($1=="diagnostics") diag=$2
  if ($1=="method3") meth3=$2
  if ($1=="method4") meth4=$2
  if ($1=="method5") meth5=$2
  if ($1=="method6") meth6=$2
  if ($1=="highlevel") highlevel=$2
  if ($1=="linkatoms") linkatoms=$2
  if ($1=="fixedatom1") fixedatom1=$2
  if ($1=="fixedatom2") fixedatom2=$2
  if ($1=="fixedatom3") fixedatom3=$2
```

```
  if ($1=="fixedatom4") fixedatom4=$2
  if ($1=="DRP") DRP=$2
  if ($1=="methodfile") methodfilelines=$2
  if ($1=="killcheck") killcheck=$2
  if ($1=="etolerance") etolerance=$2
if ($1=="reversetraj") reversetraj=$2
  if ($1=="title") {
    title1=$2
    title2=$3
    title3=$4
    title4=$5
    }
  blankLineTester=length($0)
  }

if (diag>=1) print "***************** starting prog2ndpoint ****************" >>
"diagnostics"
if (diag>=1) print "method,charge,multiplicity,memory" >> "diagnostics"
if (diag>=1) print method,charge,multiplicity,memory >> "diagnostics"
if (diag>=1) print "processors,checkpoint,title" >> "diagnostics"
if (diag>=1) print processors,checkpoint,title1,title2,title3,title4 >> "diagnostics"

#get the isomer number from file
getline < "isomernumber"
isomernum = $1

#get forward or reverse from skipstart if it exists
getline < "skipstart"
trajdirection = $1

# TO DO: rather than putting in the details here, the program should get the details from
progdyn.conf
# and progdyn.conf should have control over #proc, memory, method, basis set, etc
# though this will work for now
print " $CONTRL DFTTYP=B3PW91 RUNTYP=Gradient COORD=UNIQUE
NZVAR=0 $END"
print " $SYSTEM MWORDS=196 TIMLIM=30 $END"
print " $BASIS  GBASIS=N31 NGAUSS=6 NDFUNC=1 $END"
print " $DFT NRAD=75 NLEB=302 $END"
print " $INTGRL NINTIC=-150000000 $END"
print " $GUESS  GUESS=HUCKEL $END"
print " $DATA"
print title1,title2,title3,title4,"runpoint 2","runisomer ",isomernum
print "C1"
```

```
# ok, now we have to figure the second point.  this should be
# x(t) = x + v*t + 1/2*F*t^2/m
# so we need to set up arrays for position, velocity, and force

#read in number of atoms, geometry, masses, and velocity from geoPlusVel
getline < "geoPlusVel"
numAtoms=$1
# geometry
for (i=1;i<=numAtoms;i++) {
  getline < "geoPlusVel"
  weight[i]=$5
  atSym[i]=$1
  if (atSym[i]=="H") atNum[i]=1.0
if (atSym[i]=="Li") atNum[i]=3.0
  if (atSym[i]=="B") atNum[i]=5.0
  if (atSym[i]=="C") atNum[i]=6.0
  if (atSym[i]=="N") atNum[i]=7.0
  if (atSym[i]=="O") atNum[i]=8.0
  if (atSym[i]=="F") atNum[i]=9.0
  if (atSym[i]=="Na") atNum[i]=11.0
  for (j=1;j<=3;j++) {
    geoArr[i,j]=$(1+j)
    }
  }
#velocities
for (i=1;i<=numAtoms;i++) {
  getline < "geoPlusVel"
  for (j=1;j<=3;j++) {
    velArr[i,j]=$j
    }
  }

#now we go ahead and add the velocities
for (i=1;i<=numAtoms;i++) {
  for (j=1;j<=3;j++) {
    arr[i,j]=velArr[i,j]+geoArr[i,j]
    if (trajdirection=="reverserestart") arr[i,j]=geoArr[i,j]-velArr[i,j]
    }
  if ((diag>1) && (i==1)) print "geometry after adding velocities" >> "diagnostics"
  if (diag>1) print arr[i,1],arr[i,2],arr[i,3] >> "diagnostics"
  }

#pull out other information useful for testing whether total energy is right or bad
```

```
blankLineTester=10
while (blankLineTester>1) {
  getline < "geoPlusVel"
  if ($4=="desired=") desiredModeEnK=$5
  if ($4=="modes=") {
    KEinitmodes=$5
    KEinittotal=$9
    }
  if ($11=="potential") potentialE=$13
  blankLineTester=length($0)
  }
#get initial geometry into file traj
print numAtoms >> "traj"
print potentialE,title1,title2,title3,title4,"runpoint 1 ","runisomer ",isomernum >> "traj"
for (i=1;i<=numAtoms;i++) {
  print atSym[i],geoArr[i,1],geoArr[i,2],geoArr[i,3] >> "traj"
  }
#added by Samae on 102910
scfcount=0
} # end of BEGIN

#pull out the potential energy
/TOTAL ENERGY/ {
if ($2=="ENERGY") newPotentialE=$4
newPotentialEK=(newPotentialE-potentialE)*627.509
}

# now we go ahead and translate the forces and add them
/GRADIENT OF THE ENERGY/,/MAXIMUM GRADIENT =/ {
  if (length($5) > 9) {
    i=$1
    for (j=1;j<=3;j++) {
      forceArr[i,j]=-$(2+j)
      }
    }
if ((diag>1) && (i==1)) print "i,weight[i],forceArr[i,1],forceArr[i,2],forceArr[i,3]" >>
"diagnostics"
if (diag>1) print i,weight[i],forceArr[i,1],forceArr[i,2],forceArr[i,3] >> "diagnostics"
}

END {
#put out Echeck but only if not a DRP
if (DRP==0) {
  print "trajectory #",isomernum >> "Echeck"
```

```
  print "point 1 potential E=",newPotentialEK,"   point 1 kinetic E=",KEinittotal,"
Total=",newPotentialEK+KEinittotal >> "Echeck"
  print "desired total energy=", desiredModeEnK >> "Echeck"
  if ((newPotentialEK+KEinittotal)>(desiredModeEnK+etolerance)) print "XXXX bad
total Energy" >> "Echeck"
  if ((newPotentialEK+KEinittotal)<(desiredModeEnK-etolerance)) print "XXXX bad
total Energy" >> "Echeck"
  }
# turn the forces into motion
for (i=1;i<=numAtoms;i++) {
  for (j=1;j<=3;j++) {
# conversions here take force to J/angstrom, 1E20 converts to kg angstroms / s^2, then
mult time (s^s) and divide by weight in kg to get angstroms

forceArr[i,j]=0.5*1E20*forceArr[i,j]*627.509*(4184/(0.529177*avNum))*(timestep^2)/
(weight[i]/(avNum*1000))
# for simplicity, DRPs will throw away the forces at the second pont.  This means that if
we are not at a saddlepoint, point 2 = point 1 but this is a minor waste
     if (DRP==1) forceArr[i,j]=0
     arr[i,j]=arr[i,j]+forceArr[i,j]
# if atoms are fixed, replace calcd new position by original position
     if ((i==fixedatom1) || (i==fixedatom2) || (i==fixedatom3) || (i==fixedatom4))
arr[i,j]=geoArr[i,j]
     }
  if ((diag>1) && (i==1)) print "i,weight[i],forceArr[i,1],forceArr[i,2],forceArr[i,3]" >>
"diagnostics"
  if (diag>1) print i,weight[i],forceArr[i,1],forceArr[i,2],forceArr[i,3] >> "diagnostics"
  printf("%s %.2f %.7f %.7f %.7f",atSym[i],atNum[i],arr[i,1],arr[i,2],arr[i,3])
  print ""
  }
print " $END"
#get second geometry into file traj
print numAtoms >> "traj"
print newPotentialE,title1,title2,title3,title4,"runpoint 2 ","runisomer ",isomernum >>
"traj"
for (i=1;i<=numAtoms;i++) {
  print atSym[i],arr[i,1],arr[i,2],arr[i,3] >> "traj"
 }
}
```

Program progdynb

```
BEGIN { #this is the main routine for generating new .com files by the Verlet
algorithym
# Aug 2010 increased elements handled automatically but only up to bromine!
```

```
# Jan 2009 - a number of little changes to improve reporting, precision, etc
# Nov 2008 added ability to handle DRPs
# Aug 2008 added long list of atoms to handle 1-17 without change
# May 2008 added option to put out velocities in vellist - make diag=3
# version Feb 2008 incorporates methodfile, boxon and boxsize
# version Jan 2008 incorporates fixed atoms, oniom, and velocity damping
# version August 2007 incorporates keepevery to decrease size of dyn file
# version Sept 11, 2005 - incorportates meth3, meth4, meth5, meth6, but not yet rotation

# default parameters, including quassiclassical, no displacements, transition state, not a
DRP
# do not change these - rather, change progdyn.conf to set the parameters
initialDis=0; timestep=1E-15; scaling=1.0; temp=298.15
classical=0; numimag=1; DRP=0; cannonball=0
memory=20000000
diag=1; checkpoint="g09.chk"; searchdir="positive"; boxon=0
boxsize=10; maxAtomMove=0.1; title1="you"; title2="need"
title3="a"; title4="progdyn.conf"; processors=1; highlevel=999; linkatoms=0
damping=1

#initialization
i=1;j=1;k=1
c=29979245800; h=6.626075E-34; avNum=6.0221415E23
RgasK=0.00198588; RgasJ=8.31447
numAtoms=0; atomnumber=0
conver1=4.184E26 #dividing by this converts amu angs^2 /s^2 to kcal/mol

# read progdyn.conf for configuration info
blankLineTester=10
while (blankLineTester>1) {
  getline < "progdyn.conf"
  if ($1=="method") method=$2
  if ($1=="method2") meth2=$2
  if ($1=="charge") charge=$2
  if ($1=="multiplicity") multiplicity=$2
  if ($1=="memory") memory=$2
  if ($1=="processors") processors=$2
  if ($1=="checkpoint") checkpoint=$2
  if ($1=="timestep") timestep=$2
  if ($1=="diagnostics") diag=$2
  if ($1=="method3") meth3=$2
  if ($1=="method4") meth4=$2
  if ($1=="method5") meth5=$2
  if ($1=="method6") meth6=$2
```

```
  if ($1=="highlevel") highlevel=$2
  if ($1=="linkatoms") linkatoms=$2
  if ($1=="keepevery") keepevery=$2
  if ($1=="fixedatom1") fixedatom1=$2
  if ($1=="fixedatom2") fixedatom2=$2
 if ($1=="fixedatom3") fixedatom3=$2
  if ($1=="fixedatom4") fixedatom4=$2
  if ($1=="boxon") boxon=$2
  if ($1=="boxsize") boxsize=$2
  if ($1=="DRP") DRP=$2
  if ($1=="maxAtomMove") maxAtomMove=$2
  if ($1=="methodfile") methodfilelines=$2
  if ($1=="killcheck") killcheck=$2
  if ($1=="damping") damping=$2
  if ($1=="title") {
    title1=$2
    title2=$3
    title3=$4
    title4=$5
    }
  blankLineTester=length($0)
  }

if (diag>=1) print "***************** starting progdynb *****************" >>
"diagnostics"
if (diag>=1) print "method,charge,multiplicity,memory" >> "diagnostics"
if (diag>=1) print method,charge,multiplicity,memory >> "diagnostics"
if (diag>=1) print "processors,checkpoint,title" >> "diagnostics"
if (diag>=1) print processors,checkpoint,title1,title2,title3,title4 >> "diagnostics"

# get number of atoms and weights from geoPlusVel, and previous geometries from old
and older
getline < "geoPlusVel"
numAtoms=$1
for (i=1;i<=numAtoms;i++) {
  getline < "geoPlusVel"
  weight[i]=$5; atSym[i]=$1
  if (atSym[i]=="H") atNum[i]=1.0
  if (atSym[i]=="Li") atNum[i]=3.0
  if (atSym[i]=="B") atNum[i]=5.0
  if (atSym[i]=="C") atNum[i]=6.0
  if (atSym[i]=="N") atNum[i]=7.0
  if (atSym[i]=="O") atNum[i]=8.0
  if (atSym[i]=="F") atNum[i]=9.0
```

```
  if (atSym[i]=="Na") atNum[i]=11.0
  }

for (at=1;at<=numAtoms;at++) {
  getline < "old"
  oldarr[at,1]=$3*0.529177249; oldarr[at,2]=$4*0.529177249;
oldarr[at,3]=$5*0.529177249
  }

for (at=1;at<=numAtoms;at++) {
  getline < "older"
  olderarr[at,1]=$3*0.529177249; olderarr[at,2]=$4*0.529177249;
olderarr[at,3]=$5*0.529177249
  }

#for DRPs read in oldAdjForces and maxAtomMove
if (DRP==1) {
  for (at=1;at<=numAtoms;at++) {
    getline < "oldAdjForces"
    oldForce[at,1]=$1; oldForce[at,2]=$2; oldForce[at,3]=$3
    }
  getline < "maxMove"
  if (($1<maxAtomMove) && ($1>0)) maxAtomMove=$1
  if (maxAtomMove<0.000001) maxAtomMove=0.000001
  }

# record atom velocities for IVR analysis.  This is actually the velocity in the previous
run, which is the easiest to calculate.
getline < "isomernumber"
isomernum = $1
getline < "runpointnumber"
runpointnum = $1
if (diag==3) print "runpoint ",runpointnum-1,"runisomer ",isomernum >> "vellist"
for (at=1;at<=numAtoms;at++) {
  atomVel=((oldarr[at,1]-olderarr[at,1])^2 + (oldarr[at,2]-olderarr[at,2])^2
+(oldarr[at,3]-olderarr[at,3])^2)^.5
  KEatomstotal=KEatomstotal+0.5*weight[at]*(atomVel^2)/((timestep^2)*conver1)
  if (diag==3) print atomVel >> "vellist"
  }
apparentTemp=KEatomstotal*2/(3*RgasK*numAtoms)
if (diag==4) print "KEatomstotal",KEatomstotal,"apparent Temperature",apparentTemp
>> "vellist"
}
```

```
#pull out the potential energy
/TOTAL ENERGY/ {
if ($2=="ENERGY") newPotentialE=$4
}

#now pull out the forces
/GRADIENT OF THE ENERGY/,/MAXIMUM GRADIENT =/ {
  if (length($5) > 9) {
    i=$1
for (j=1;j<=3;j++) {
       forceArr[i,j]=-$(2+j)
       }
    }
if ((diag>1) && (i==1)) print "i,weight[i],forceArr[i,1],forceArr[i,2],forceArr[i,3]" >>
"diagnostics"
if (diag>1) print i,weight[i],forceArr[i,1],forceArr[i,2],forceArr[i,3] >> "diagnostics"
}

END {
##############routine for DRPs###############
if (DRP==1) {
  maxForce=0;oscillTest=0
  for (i=1;i<=numAtoms;i++) {
    for (j=1;j<=3;j++) {
# conversions here take force to J/angstrom, 1E20 converts to kg angstroms / s^2, then
mult time (s^s) and divide by weight in kg to get angstroms

forceArr[i,j]=1E20*forceArr[i,j]*627.509*(4184/(0.529177*avNum))*(timestep^2)/(wei
ght[i]/(avNum*1000))
       oscillTest=oscillTest+forceArr[i,j]*oldForce[i,j]
       if (forceArr[i,j]>maxForce) maxForce=forceArr[i,j]
       if ((0-forceArr[i,j])>maxForce) maxForce=-forceArr[i,j]
       }
    if (i==1) printf("% .8f % .8f % .8f \n",forceArr[1,1],forceArr[1,2],forceArr[1,3])  >
"oldAdjForces"
    if (i>1) printf("% .8f % .8f % .8f \n",forceArr[i,1],forceArr[i,2],forceArr[i,3])  >>
"oldAdjForces"
    }
  print "oscillTest ",oscillTest >> "oldAdjForces"
  if (oscillTest<0) {
    maxAtomMove = maxAtomMove*0.5
    print maxAtomMove > "maxMove"
    }
  if (oscillTest>0) {
```

```
    maxAtomMove = maxAtomMove*1.2
    print maxAtomMove > "maxMove"
    }
  print "maxAtomMove ",maxAtomMove >> "oldAdjForces"
  forceMult=maxAtomMove/maxForce
  for (i=1;i<=numAtoms;i++) {
    for (j=1;j<=3;j++) {
      newarr[i,j]=oldarr[i,j]+forceMult*forceArr[i,j]
      }
    }
  }
########

##############normal routine for Verlet ###############
if (DRP==0) {
  for (i=1;i<=numAtoms;i++) {
    for (j=1;j<=3;j++) {
# conversions here take force to J/angstrom, 1E20 converts to kg angstroms / s^2, then
mult time (s^s) and divide by weight in kg to get angstroms

forceArr[i,j]=1E20*forceArr[i,j]*627.509*(4184/(0.529177*avNum))*(timestep^2)/(wei
ght[i]/(avNum*1000))
      if ((diag>1) && (i==1)) print "i,weight[i],forceArr[i,1],forceArr[i,2],forceArr[i,3]"
>> "diagnostics"
      if (diag>1) print i,weight[i],forceArr[i,1],forceArr[i,2],forceArr[i,3] >>
"diagnostics"
newarr[i,j]=oldarr[i,j]+damping*(oldarr[i,j]-olderarr[i,j])+forceArr[i,j]
      if ((i==fixedatom1) || (i==fixedatom2) || (i==fixedatom3) || (i==fixedatom4))
newarr[i,j]=oldarr[i,j]
#turn around atoms outside the box
      if (boxon==1) {
        if (newarr[i,j]>boxsize) if (oldarr[i,j]>olderarr[i,j])
newarr[i,j]=oldarr[i,j]+damping*(olderarr[i,j]-oldarr[i,j])+forceArr[i,j]
        if (newarr[i,j]<-1*boxsize) if (oldarr[i,j]<olderarr[i,j])
newarr[i,j]=oldarr[i,j]+damping*(olderarr[i,j]-oldarr[i,j])+forceArr[i,j]
        }
      }
    }
  }
########

if ((runpointnum % keepevery)==0) system("cat gamess.log >> dyn")
# TO DO: rather than putting in the details here, the program should get the details from
progdyn.conf
```

```
# and progdyn.conf should have control over #proc, memory, method, basis set, etc
# though this will work for now
print " $CONTRL DFTTYP=B3PW91 RUNTYP=Gradient COORD=UNIQUE
NZVAR=0 $END"
print " $SYSTEM MWORDS=196 TIMLIM=30 $END"
print " $BASIS  GBASIS=N31 NGAUSS=6 NDFUNC=1 $END"
print " $DFT NRAD=75 NLEB=302 $END"
print " $INTGRL NINTIC=-150000000 $END"
print " $GUESS  GUESS=HUCKEL $END"
print " $DATA"
print title1,title2,title3,title4" runpoint "runpointnum" runisomer "isomernum
print "C1"
print numAtoms >> "traj"
print newPotentialE,title1,title2,title3,title4,"runpoint ",runpointnum,"runisomer
",isomernum >> "traj"
for (i=1;i<=numAtoms;i++) {
  printf("%s %.2f %.7f %.7f
%.7f",atSym[i],atNum[i],newarr[i,1],newarr[i,2],newarr[i,3])
  printf("%s %.7f %.7f %.7f",atSym[i],newarr[i,1],newarr[i,2],newarr[i,3]) >> "traj"
  print "" >> "traj"
  print ""
  }
print " $END"
print ""
}
```

Program randgen

The c code for randgen is given below, and this may be compiled to form the program randgen.

```
#include <stdio.h>
#include <stdlib.h>
int a,b,c;
double d;
int product(int x, int y);
int main(void)
{
int count=1;
srand48(time (0));
while (count<=100000)
{
d = drand48();
printf ("%.20f\n", d);
count++;
}
```

```
return 0;
}
```

Program proganal

The version of proganal shown below was used for the trajectories for the thermal dimerization reaction of 1. Proganal was modified to keep track of the interatomic distances in the forming bonds (using lines "short=Distance(1,11)" and "long=Distance(6,10)"), and the stopping criteria for recrossing and for product formation were "if ((short>2.3) && (long>2.5)) {" and "if ((short<1.8) && (long<2.0)) {", respectively

```
BEGIN {
firsttitle=1
getline < "isomernumber"
isomer=$1
atomNum=1
}
/metha/ {
  if (firsttitle==2) {
    printf("%s %s %s %s %s %s %s  ",$1,$2,$3,$4,$6,$7,$8)
    runpoint=$6
    }
  firsttitle++
  }
/ATOM     ATOMIC                    COORDINATES/,/INTERNUCLEAR
DISTANCES/ {
  if (($2>.5) && ($2<120)) {

A[atomNum]=$3*0.529177249;B[atomNum]=$4*0.529177249;C[atomNum]=$5*0.529
177249
    atomNum++
    }
  }

END {
  C5C12=Distance(5,12)
  C1O11=Distance(1,11)
  O3C8=Distance(3,8)
  printf("%s %.3f %s %.3f %s %.3f ","C5C12",C5C12,"C1O11",C1O11,"O3C8",O3C8)
  if ((C5C12<1.7) && (O3C8<1.9)) {
    print "Formed prod1 XXXX"
#    system("date > nogo")
    }
  if ((C5C12<1.7) && (C1O11<1.9)) {
```

```
    print "Formed prod2 XXXX"
#    system("date > nogo")
    }
  if (runpoint>500) {
    print "   Too many points.  XXXX"
    }
#    if (runpoint<20) {
#    system("date > nogo")
#    }
  if ((C5C12>2.4) && (O3C8>2.4) && (C1O11>2.4)) {
    print "Returned to SM XXXX"
    }
  system("date '+%b:%d:%Y %T'")
  system("tail -1 Echeck | grep XXXX")
  }

function Distance(Atom1,Atom2) {
 return sqrt((A[Atom1]-A[Atom2])^2 + (B[Atom1]-B[Atom2])^2 + (C[Atom1]-
C[Atom2])^2)
}
function Distance(Atom1,Atom2) {
 return sqrt((A[Atom1]-A[Atom2])^2 + (B[Atom1]-B[Atom2])^2 + (C[Atom1]-
C[Atom2])^2)
}

function Angle(Atom1,Atom2,Atom3) {
  value=((-
Distance(Atom1,Atom3)^2+Distance(Atom1,Atom2)^2+Distance(Atom2,Atom3)^2)/(2
*Distance(Atom1,Atom2)*Distance(Atom2,Atom3)))
  return acos(value)
}

function asin(x) { return (180/3.141592)*atan2(x, sqrt(1-x*x)) }

function acos(x) { return (180/3.141592)*atan2(sqrt(1-x*x), x) }

function atan(x) { return (180/3.141592)*atan2(x,1) }

function Dihedral(Atom1,Atom2,Atom3,Atom4) {
  B1x=A[Atom2]-A[Atom1]
  B1y=B[Atom2]-B[Atom1]
  B1z=C[Atom2]-C[Atom1]
  B2x=A[Atom3]-A[Atom2]
  B2y=B[Atom3]-B[Atom2]
```

```
  B2z=C[Atom3]-C[Atom2]
  B3x=A[Atom4]-A[Atom3]
  B3y=B[Atom4]-B[Atom3]
  B3z=C[Atom4]-C[Atom3]
  modB2=sqrt((B2x^2)+(B2y^2)+(B2z^2))
# yAx is x-coord. etc of modulus of B2 times B1
  yAx=modB2*(B1x)
  yAy=modB2*(B1y)
  yAz=modB2*(B1z)
# CP2 is the crossproduct of B2 and B3
  CP2x=(B2y*B3z)-(B2z*B3y)
  CP2y=(B2z*B3x)-(B2x*B3z)
  CP2z=(B2x*B3y)-(B2y*B3x)
  termY=((yAx*CP2x)+(yAy*CP2y)+(yAz*CP2z))
# CP is the crossproduct of B1 and B2
  CPx=(B1y*B2z)-(B1z*B2y)
  CPy=(B1z*B2x)-(B1x*B2z)
  CPz=(B1x*B2y)-(B1y*B2x)
  termX=((CPx*CP2x)+(CPy*CP2y)+(CPz*CP2z))
 dihed4=(180/3.141592)*atan2(termY,termX)
 return dihed4
}

function killdyn(isomer) {
  system("rm -f dyn")
}
```

Program progdyn.conf

The progdyn.conf below is the one used for quasiclassical trajectories for the thermal dimerization reaction of 1 with a 16C in carbon b (see main text) in one of the molecules of 1. Other calculations would differ in obvious ways in the lines labeled title and charge. The line labeled classical was changed from "classical 0" to "classical 1" for fully classical simulations.

```
#This is the configuration file for PROGDYN.  This file is read by progdyngamess and
# the awk programs proggenHP, prog1stpoint, prog2ndpoint, and progdynb.
#The programs won't read anything past the first blank line,
#and this file must end with a blank line.
#The program has a number of default values but they are unlikely to be what you want.
#Do not delete lines - rather, comment out lines for unwanted options.
#The values here are read repeatedly and most can be changed in the middle of running
jobs
#***The keywords are case sensitive.  The following keywords should always be
defined:***
```

```
#***method, charge, multiplicity, memory, processors, title
#*** method --The following word is copied exactly to the gaussian input file.
method B3PW91/6-31G*
#*** method2 --The options here are restricted, unrestricted, and read. restricted is the
default
#If the method is U..., put unrestricted here and the .com files will have in them
guess=mix.
#If you put read here, the .com files will contain guess=tcheck, which sometimes makes
things faster, sometimes not.
#The use of read requires a specifically defined checkpoint file name using the keyword
checkpoint.
method2 restricted
charge 0
multiplicity 1
processors 2
#*** memory --The following "word" is copied exactly to the gaussian input file after
%mem=.
memory 200mw
#*** killcheck and checkpoint -- You can use a specifically defined checkpoint file
name by putting
#the name after the keyword checkpoint.  This is necessary if you use the read option
with method2.
#Defined checkpoint names are an unnecessary modest hastle and if you do not want to
bother, use killcheck 1
killcheck 1
#checkpoint dyn20.chk
#*** diagnostics -- 0 prints out nothing extra, 1 (default) prints out extra stuff to a
#file "diagnostics", 2 adds more stuff, 3 adds velocities to a file "vellist"
#4 adds the apparent temperature to vellist, but this is meaningless with quasiclassical
calculations
diagnostics 0
#*** title -- the title keyword must be followed by exactly four words
title methacrolein C116 B3PW91 343dis2
#*** initialdis -- 0 (default) turns off displacement of the normal modes, so that all
trajectories start from the same place
# and only the energies and signs of the motion in the modes are randomized
# 1 gives a flat distribution of displacements where all of the possible values are equally
likely
# 2 (recommended) gives a QM-like gaussian distribution of displacements, so that
displacements in the middle are more likely that
# those at the end by 1/e
initialdis 2
#*** timestep -- this is the time between points in the trajectory.  Typical values would
be 1E-15 or 0.5E-15 or 0.25E-15
```

```
timestep 1E-15
#*** scaling -- this lets you scale the gaussian frequencies by a constant
scaling 1.0
temperature 343.15
#*** method3, method4, method5, and method6 -- These keywords let you add extra lines to the gaussian input file.
#method3 and method4 add lines at the top of the input after the lines defining the method, and
#this is useful to implement things like the iop for mPW1k
#method5 and method6 add lines after the geometry, after a blank line of course
#only a single term with no spaces can be added, one per method line.  Here are some examples to uncomment if needed
#method3 IOp(3/76=0572004280)
#method3 scrf=(pcm,Solvent=water)
#add the line below with big structures to get it to put out the distance matrix and the input orientation
#method3 iop(2/9=2000)
#method4 scrf=(pcm,solvent=dmso,read)
#method5 radii=bondi
#method6
#*** methodfile -- This keyword lets you add more complicated endings to gaussian input files
#such as a gen basis set.  Put after the keyword the number of lines in a file you create called
#methodfile that contains the test you want to add to the end of the gaussian input
methodfile 0
#*** numimag --This tells the program the number of imaginary frequencies in the starting structure.
#if 0, treats as ground state and direction of all modes is random
#if 1, motion along the reaction coordinate will start out in the direction defined by searchdir
#if 2, only lowest freq will go direction of searchdir and other imag mode will go in random direction
numimag 1
#*** searchdir -- This keyword says what direction to follow the mode associated with the imaginary frequency.
#The choices are "negative" and "positive".  Positive moves in the direction defined in the gaussian frequency calculation
#for the imaginary frequency, while negative moves in the opposite direction.  The correct choice can be made either
#by a careful inspection of the normal modes and standard orientation geometry, or by trial and error.
searchdir negative
```

#*** classical -- for quassiclassical dynamics, the default, use 0. for classical dynamics, use 1
#if there are no normal modes and the velocities are to be generated from scratch, use classical 2
classical 0
#*** DRP, saddlepoint, and maxAtomMove --to run a DRP use 'DRP 1' in the line below, otherwise leave it at 0 or comment it out
#the treatment of starting saddlepoints is not yet implemented so use saddlepoint no
#if DRP shows oscillations then decrease maxAtomMove
#DRP 1
#saddlepoint no
#maxAtomMove 0.01
#*** cannonball -- The program can "fire" a trajectory from a starting position toward a particular target, such as toward
#a ts. To use this, make a file cannontraj with numAtom lines and three numbers per line that defines the vector
#for firing the trajectory, relative to the starting geometry's standard orientation. The number following cannonball sets
#the extra energy being put into the structure in kcal/mol
#cannonball 10
#*** keepevery --This tells the program how often to write the gaussian output file to file dyn, after the first two points.
#Use 1 for most dynamics to start with, but use a higher number to save on disk space or molden loading time.
keepevery 99
#*** highlevel --For ONIOM jobs, the following line states the number of highlevel atoms,
#which must come before the medium level atoms. Use some high value such as 999 if not using ONIOM
highlevel 999
#*** fixedatom1, fixedatom2, fixedatom3, and fixedatom4 - These fix atoms in space.
#Fixing one atom serves no useful purpose and messes things up, while fixing two atoms
#fixes one distance and fixing three has the effect of fixing three distances, not just two
#in current form fixed atoms only are meant to work with no displacements, that is, initialdis=0
#fixedatom1 2
#fixedatom2 3
#fixedatom3 19
#*** boxon and boxsize - With boxon 1, a cubic box is set such that atoms that reach the edge
#are reflected back toward the middle. Useful for dynamics with solvent molecules. This is a crude
#implementation that is ok for a few thousand femtoseconds but will not conserve energy long term.

#Set the box size so as to fit the entire initial molecule but not have too much extra room.
#The dimensions of the box are two times the boxsize, e.g. boxsize 7.5 leads to a box that is 15 x 15 x 15 angstroms
boxon 0
boxsize 7.5
#*** displacements -- This keyword lets you set the initialdis of particular modes by using a series of lines of the format
displacements NumberOfMode InitialDisForThatMode, as in the example below. You should be able to do as many of these as you like
you might consider this for rotations where a straight-line displacement goes wrong at large displacements
The choices for InitialDisForThatMode are 0, 1, 2, and 10, where 10 does the same thing as 0 but is maintained for now because
a previous version of the program had a bug that made 0 not work.
#displacements 2 0
#displacements 3 0
#*** etolerance --This sets the allowable difference between the desired energy in a trajectory and the actual
#energy, known after point 1 from the potential energy + the kinetic energy in the initial velocities.
#The unit is kcal/mol and 1 is a normal value for mid-sized organic systems. For very large and floppy molecules, a larger value
#may be needed, but the value must stay way below the average thermal energy in the molecule (not counting zpe).
#If initialdis is not 0 and few trajectories are being rejected, decrease the value.
etolerance 1
#*** controlphase --It is sometimes useful to set the phase of particular modes in the initialization of trajectories.
#The format is controlphase numberOfModeToControl positive or controlphase numberOfModeToControl negative.
controlphase 2 positive
#*** damping -- The damping keyword lets you add or subtract energy from the system at each point, by multiplying the velocities
#by the damping factor. A damping of 1 has no effect, and since you mostly want to change the energy slowly, normal values range
#from 0.95 to 1.05. The use of damping lets one do simulated annealing - you add energy until the structure is moving enough
#to sample the kinds of possibilities you are interested in, then you take away the energy slowly.
damping 1
#*** reversetraj --This keyword sets the trajectories so that both directions from a transition state are explored.
#reversetraj true

#updated Aug 9, 2007 to include the possibility of classical dynamics by the keyword classical
#updated Jan 2008 to include fixed atoms, ONIOM jobs, keepevery, and box size
#update Feb 2008 to include methodfile parameter
updated Nov 2008 to allow for start without an initial freq calc using classical = 2
update Aug 2010 to include etolerance, damping controlphase and reversetraj